Contents

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 Bruker Avance III 800 (with a 5-mm CPTXI cryoprobe) and Bruker Fourier 300. Chemical shifts were reported relative to residue peaks $CDCl_3$ (7.27 ppm for ^1H and 77.0 ppm for ^{13}C) or DMSO-d_6 (2.51 ppm: for ^1H and 39.5 ppm: for ^{13}C).

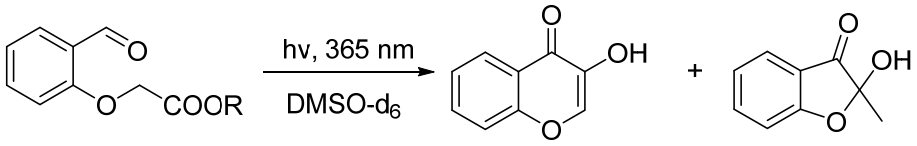
Melting points were measured on a SMP 30 apparatus without correction.

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 µl/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. IUPAC compound names were generated using ChemDraw Software.

Photocyclization processes were performed on Evoluchem™ PhotoRedOx box. 365 nm (LG, HCK1012-01-006, 25 mW/cm^2) light-emitting diode (LED) lamp from Evoluchem™ was used. This device is equipped with a fan to maintain room temperature during the irradiation process.

2. Initial research

2.1. Transformation in DMSO-d_6



1a: R = Me
2a: R = Et
3a: R = iPr
4a: R = tBu
5a: R = H

6a **7a**

Compound **1a-5a** (0.03 mmol) was dissolved in 1 mL of DMSO-d_6 in a Schlenk vessel. The mixture was degassed under vacuum and filled with argon, the procedure was repeated three times. Next, 0.65 mL of the solution was transferred to an NMR tube under argon and sealed. NMR tubes with these solutions were irradiated with 365 nm LED lamp in Evoluchem™ PhotoRedOx box for 4 h. The mixtures were analyzed by ^{1}H NMR. TMS signal was used as an internal standard - for all spectra its integral area was set on equal value. Initial integral area of aldehyde singlet signal from 10.25 ppm to 10.75 ppm was determined as 100%. The yields of components (presented on Scheme 2) were determined using the following integral areas:

- doublet signal from 8.04 ppm to 8.16 ppm (1H) for product **6a**
- singlet from 1.37 ppm to 1.54 ppm (3H) for product **7a**

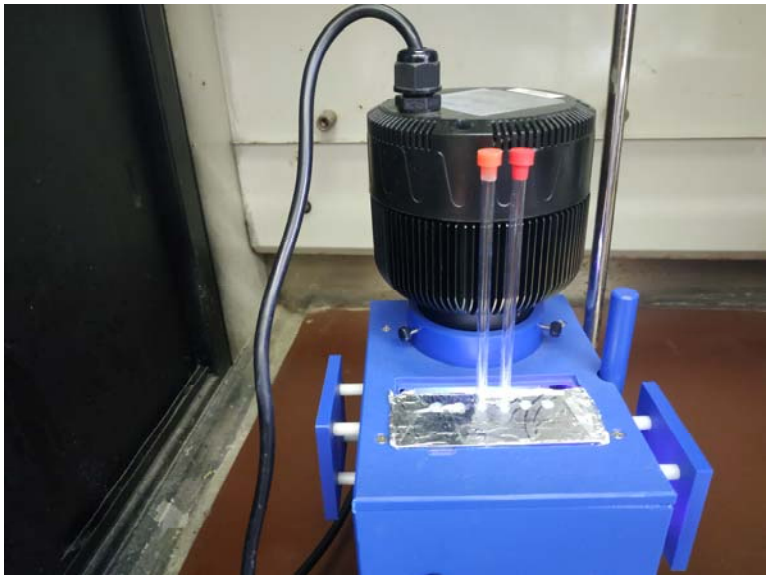
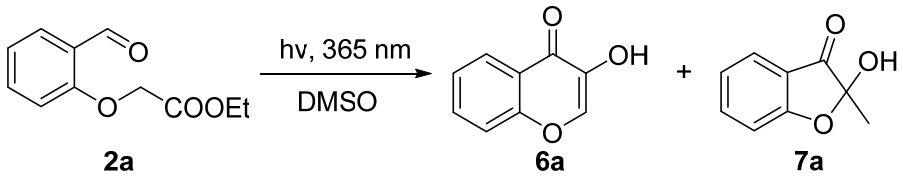


Figure S2. Photochemical set-up in NMR tubes.

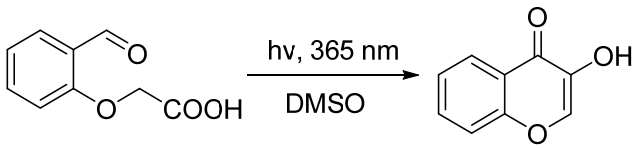
2.2. Scale-up test



2a **6a** **7a**

Compound **2a** (208 mg, 1.0 mmol) was dissolved in freshly distilled 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 for 24 h.

The reaction mixture was 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). Yield of **6a** 64 mg (40%), yield of **7a** 34 mg (21%). ^1H, ^{13}C and HRMS data are presented below (Part 5).

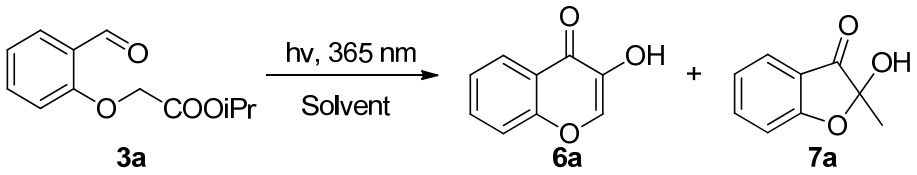


5a **6a**

Compound **5a** (180 mg, 1.0 mmol) was dissolved in freshly distilled 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 reaction mixture was 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). Yield 82 mg (51%).^1H, ^{13}C and HRMS data presented below (Part 5).

Figure 3. Photochemical set-up. Examples of large-scale reactions.

3. Optimization study



3a **6a** **7a**

Isopropyl 2-(2-formylphenoxy)acetate **3a** (22 mg, 0.1 mmol) was dissolved in freshly distilled solvent under argon atmosphere (2.0 mL). Vials, prefilled with argon, with the obtained solutions were irradiated with 365 nm LED lamp in Evoluchem™ PhotoRedOx box with stirring. Control experiment (#20) was carried out without argon. After 6 hours of irradiation, solvents were removed in vacuum. 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 Na_2SO_4 and similarly evaporated. Finally, all residues were analyzed by ^{1}H NMR in DMSO-*d*$_6$. The overall aromatic signal from 6.50 ppm to 8.18 ppm (4H) was used as a standard (400%). The quantity of components was assessed using the following signals:

- singlet from 10.25 ppm to 10.75 ppm (1H) for the starting aldehyde **3a**.
- doublet signal from 8.04 ppm to 8.16 ppm (1H) for product **6a**
- singlet from 1.37 ppm to 1.54 ppm (3H) for product **7a**

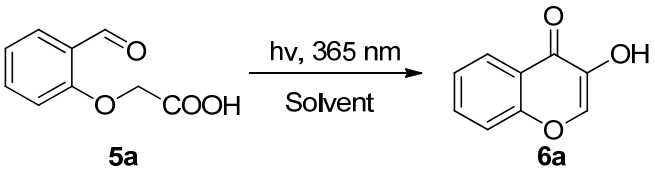
Results are presented in Table S1.

Table S1. Solvents screening results for **3a**.

Entry	Solvent	**6a**, %	**7a**, %	Unreacted **3a**, %
1	$C_2H_4Cl_2$	0	0	48
2	CH_2Cl_2	0	0	34
3	$CHCl_3$	0	0	38
4	CCl_4	0	0	11
5	MeOH	0	0	0
6	EtOH	0	0	0
7	*i*-PrOH	0	0	0
8	Acetone	0	0	16
9	CF_3CH_2OH	0	0	67
10	THF	0	0	0
11	1,4-Dioxane	0	0	0
12	Et_2O	0	0	0
13	EtOAc	0	0	0
14	CH_3CN	0	0	22
15	C_6H_6	0	0	21
16	Toluene	0	0	0
17	PhCl	0	0	8
18	Hexane	0	0	100
19	**DMSO**	**28**	**34**	**0**
20	DMSO*	20	18	0
21	DMSO**	24	32	0
22	DMF	0	0	0
23	DMA	0	0	8
24	NMP	0	0	0
25	Pyridine	0	0	5

* no argon atmosphere

** 50 mg of 5Å sieves and 50 mg of 4Å sieves were added



5a **6a**

2-(2-Formylphenoxy)acetic acid **5a** (18 mg, 0.1 mmol) was dissolved in freshly distilled solvent under argon atmosphere (2.0 mL). Vials, prefilled with argon, with the obtained solutions were irradiated with 365 nm LED lamp in Evoluchem™ PhotoRedOx box with stirring. Control experiment (#20) was carried out without argon. After 6 hours of irradiation, solvents were removed in vacuum. 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 Na_2SO_4 and similarly evaporated. Finally, all the residues were analyzed by ^{1}H NMR in DMSO-*d*$_6$ similarly to the mentioned above.

Results are presented in Table S2.

Table S2. Solvents screening results for **5a**.

Entry	Solvent	**6a**, %	Unreacted **5a**, %
1	$C_2H_4Cl_2$	0	0
2	CH_2Cl_2	0	0
3	$CHCl_3$	0	0*
4	CCl_4	0	100
5	MeOH	0	55
6	EtOH	0	0
7	*i*-PrOH	0	0
8	Acetone	0	0
9	CF_3CH_2OH	0	15
10	THF	0	0
11	1,4-Dioxane	0	0
12	Et_2O	0	0
13	EtOAc	0	0
14	CH_3CN	0	0
15	C_6H_6	0	15
16	Toluene	0	50
17	PhCl	0	20
18	Hexane	0	100
19	**DMSO**	**64**	**2**
20	DMSO**	49	0
21	DMSO***	61	0
22	DMF	0	0
23	DMAC	0	0
24	NMP	0	0
25	Pyridine	0	5

* 25% of 2-methoxybenzaldehyde were observed
** no argon atmosphere
*** 50 mg of 5Å sieves and 50 mg of 4Å sieves were added

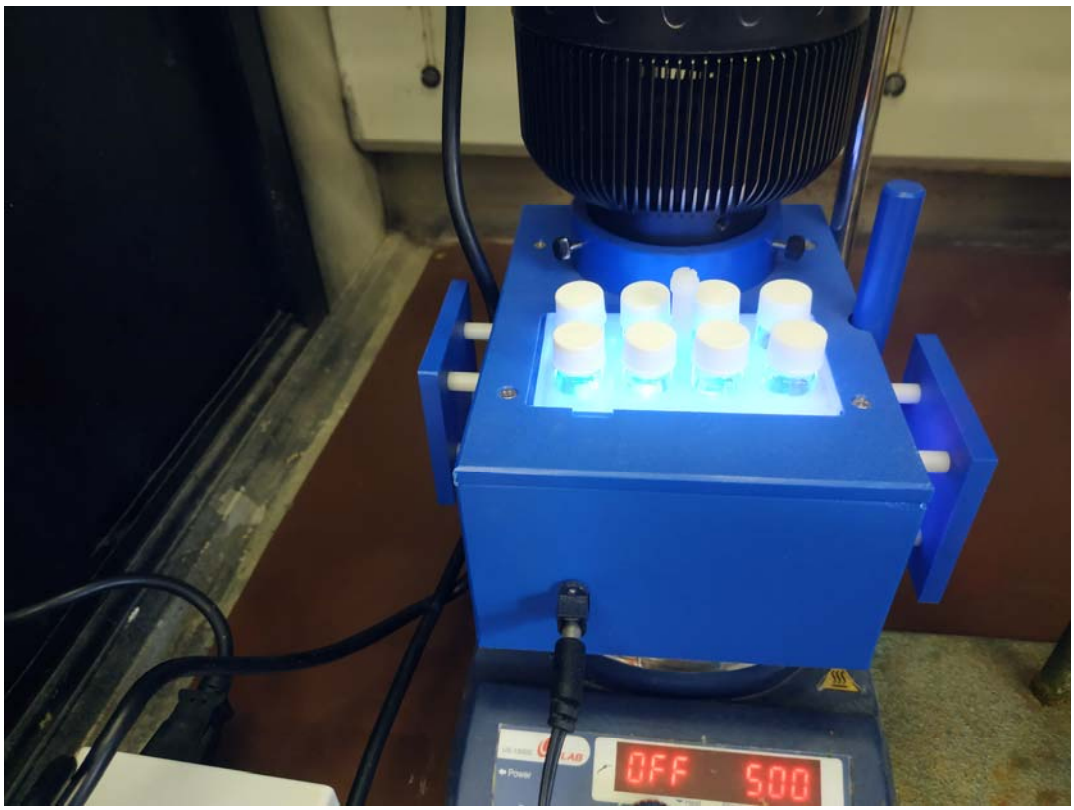


Figure S1. Photochemical set-up. Solvent screening.

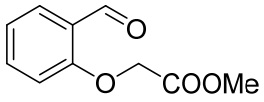
4. Synthesis of the starting compounds

4.1 Synthesis of 2-(2-formylphenoxy)acetate esters 1-4

General method

A mixture of the corresponding 2-hydroxybenzaldehyde (10 mmol), bromoacetic ester (13 mmol) and K_2CO_3 (2.76 g, 20 mmol) in freshly distilled DMF (50 mL) was heated at 80 °C for 4 h. EtOAc (200 mL) was added and the resulting mixture was washed with brine (3×50 mL). Organic layer was dried over anhydrous 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 20:1. The R_f values presented below are given for this eluent.).

Methyl 2-(2-formylphenoxy)acetate (1a)

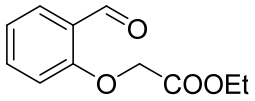


Yield 1.80 g (93%).

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 3.72 (s, 3H), 5.01 (s, 2H), 7.13 (t, *J*=7.5 Hz, 1H), 7.18 (d, *J*=8.4 Hz, 1H), 7.64 (ddd, *J*=8.6, 7.1, 1.8 Hz, 1H), 7.72 (dd, *J*=7.7, 1.8 Hz, 1H), 10.44 (s, 1H).

The spectral properties corresponded to the literature data.[1]

Ethyl 2-(2-formylphenoxy)acetate (2a)

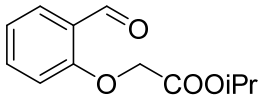


Yield 1.67 g (81%).

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 1.21 (t, *J*=7.1 Hz, 3H), 4.18 (q, *J*=7.1 Hz, 2H), 4.99 (s, 2H), 7.12 (t, *J*=7.5 Hz, 1H), 7.18 (d, *J*=8.4 Hz, 1H), 7.64 (ddd, *J*=8.6, 7.1, 1.9 Hz, 1H), 7.72 (dd, *J*=7.7, 1.8 Hz, 1H), 10.45 (s, 1H).

The spectral properties corresponded to the literature data.[2]

Isopropyl 2-(2-formylphenoxy)acetate (3a)



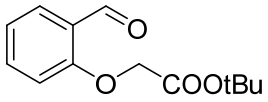
Yield 2.08 g (94%), white solid, m. p. 64-66 °C. R_f = 0.09.

^{1}H NMR (800 MHz, $CDCl_3$) δ ppm: 1.28 (d, *J*=6.3 Hz, 6H), 4.73 (s, 2H), 5.15 (spt, *J*=6.2 Hz, 1H), 6.87 (d, *J*=8.3 Hz, 1H), 7.10 (t, *J*=7.4 Hz, 1H), 7.50 - 7.57 (m, 1H), 7.86 - 7.91 (m, 1H), 10.59 (s, 1H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 21.4, 65.5, 68.6, 114.0, 121.5, 124.7, 127.5, 136.1, 160.1, 167.8, 189.0.

HRMS (ESI-TOF) found, m/z: 223.0963 $[M+H]^+$. $C_{12}H_{15}O_4^+$. Calculated, m/z: 223.0965.

Tert-butyl 2-(2-formylphenoxy)acetate (4a)

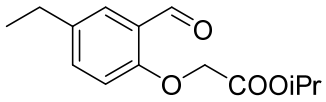


Yield 1.98 g (84%).

^{1}H NMR (800 MHz, $CDCl_3$) δ ppm: 1.49 (s, 9H), 4.66 (s, 2H), 6.86 (d, *J*=8.3 Hz, 1H), 7.09 (t, *J*=7.3 Hz, 1H), 7.54 (t, *J*=7.8 Hz, 1H), 7.88 (d, *J*=7.6 Hz, 1H), 10.58 (s, 1H).

The spectral properties corresponded to the literature data.[3]

Isopropyl 2-(4-ethyl-2-formylphenoxy)acetate (3b)



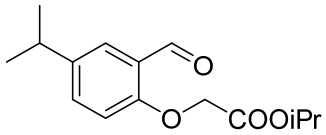
Yield 1.62 g (65%), white solid, m. p. 38-40 °C. R_f = 0.14.

^{1}H NMR (800 MHz, $CDCl_3$) δ ppm: 1.23 (t, *J*=7.6 Hz, 3H), 1.28 (d, *J*=6.3 Hz, 6H), 2.63 (q, *J*=7.6 Hz, 2H), 4.70 (s, 2H), 5.15 (spt, *J*=6.3 Hz, 1H), 6.79 (d, *J*=8.4 Hz, 1H), 7.36 (d, *J*=8.4 Hz, 1H), 7.71 (s, 1H), 10.56 (s, 1H).

^{13}C NMR (201 MHz, $CDCl_3$) δ ppm: 15.4, 21.7, 27.8, 66.1, 69.4, 112.8, 125.3, 127.4, 135.2, 137.7, 158.5, 167.9, 189.8.

HRMS (ESI-TOF) found, m/z: 251.1278 $[M+H]^+$. $C_{14}H_{19}O_4^+$. Calculated, m/z: 251.1278.

Isopropyl 2-(2-formyl-4-isopropylphenoxy)acetate (3c)



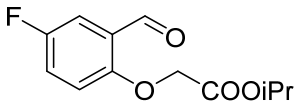
Yield 2.30 g (87%), white solid, m. p. 40-42 °C. R_f = 0.12.

^{1}H NMR (800 MHz, $CDCl_3$) δ ppm: 1.24 (d, *J*=6.9 Hz, 6H), 1.28 (d, *J*=6.3 Hz, 6H), 2.91 (spt, *J*=6.8 Hz, 1H), 4.70 (s, 2H), 5.08 - 5.20 (m, *J*=6.2, 6.2, 6.2, 6.2, 6.2, 6.1 Hz, 1H), 6.80 (d, *J*=8.5 Hz, 1H), 7.40 (dd, *J*=8.5, 2.1 Hz, 1H), 7.74 (d, *J*=2.1 Hz, 1H), 10.56 (s, 1H).

^{13}C NMR (201 MHz, $CDCl_3$) δ ppm: 21.7, 23.8, 33.2, 66.1, 69.4, 112.7, 125.3, 126.0, 133.9, 142.4, 158.6, 167.9, 189.9.

HRMS (ESI-TOF) found, m/z: 265.1434 $[M+H]^+$. $C_{15}H_{21}O_4^+$. Calculated, m/z: 265.1434.

Isopropyl 2-(4-fluoro-2-formylphenoxy)acetate (3g)



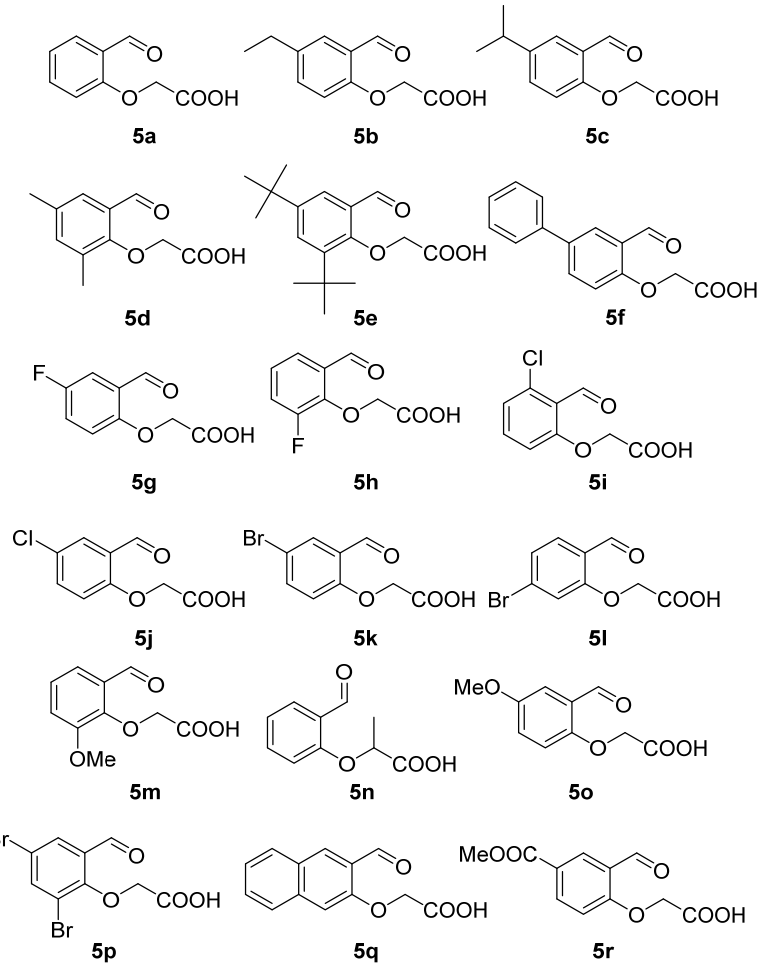
Yield 2.25 g (94%), white solid, m. p. 48-50 °C. R_f = 0.10.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 1.20 (d, *J*=6.3 Hz, 6H), 4.96 (s, 2H), 4.99 (spt, *J*=6.3 Hz, 1H), 7.26 (dd, *J*=9.2, 4.0 Hz, 1H), 7.43 (dd, *J*=8.4, 3.3 Hz, 1H), 7.53 (td, *J*=8.6, 3.3 Hz, 1H), 10.39 (d, *J*=3.1 Hz, 1H).

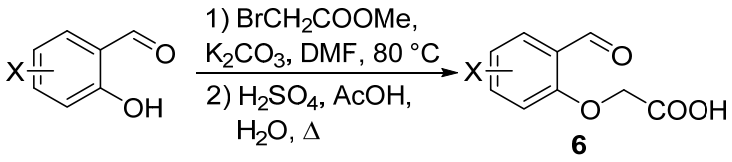
^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 21.4, 66.2, 68.6, 112.8 (d, *J*=23.5 Hz), 116.6 (d, *J*=7.5 Hz), 122.7 (d, *J*=23.9 Hz), 125.7 (d, *J*=5.9 Hz), 156.6 (d, *J*=1.5 Hz), 156.7 (d, *J*=239.9 Hz), 167.8, 188.3 (d, *J*=14.1 Hz).

HRMS (ESI-TOF) found, m/z: 241.0872 $[M+H]^+$. $C_{12}H_{14}FO_4^+$. Calculated, m/z: 241.0871.

4.2 Synthesis of 2-(2-formylphenoxy)acetic acids 5

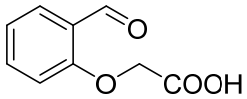


General method (5a-5m, 5o-5q)



A mixture of the corresponding 2-hydroxybenzaldehyde (10 mmol), methyl bromoacetate (1.99 g, 13 mmol) and K_2CO_3 (2.76 g, 20 mmol) in freshly distilled DMF (50 mL) was heated at 80 °C for 4 h. EtOAc (200 mL) was added and the resulting mixture was washed with brine (3×50 mL). Organic layer was dried over anhydrous Na_2SO_4, all volatiles were removed in vacuo and the residue was dissolved in the mixture of 25 mL of AcOH, 20 mL of water and 7.5 mL of H_2SO_4. The resulting mixture was refluxed for 4 h, cooled to the RT, diluted with 200 mL of brine and extracted with CH_2Cl_2 (3×100 mL). Combined layers were washed with brine (10×30 mL) and dried over Na_2SO_4. All volatiles were removed in vacuo and the residue was purified with flash chromatography (Eluent – EtOAc. The R_f values presented below are given for this eluent. Short pads of silicagel were used, since the compounds are very polar.).

2-(2-Formylphenoxy)acetic acid (5a)

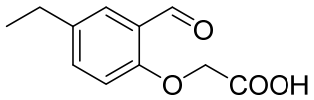


Yield 1.44 g (80%).

^{1}H NMR (800 MHz, DMSO-*d*$_6$) δ ppm: 4.88 (s, 2H), 7.11 (t, *J*=7.4 Hz, 1H), 7.15 (d, *J*=8.4 Hz, 1H), 7.59 - 7.67 (m, 1H), 7.71 (dd, *J*=7.6, 1.6 Hz, 1H), 10.45 (br. s., 1H).

The spectral properties corresponded to the literature data.[4]

2-(4-Ethyl-2-formylphenoxy)acetic acid (5b)



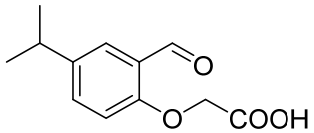
Yield 1.02 g (49%), white solid, m. p. 126-128 °C. R_f = 0.08.

^{1}H NMR (800 MHz, DMSO-*d*$_6$) δ ppm: 1.16 (t, *J*=7.6 Hz, 3H), 2.59 (q, *J*=7.6 Hz, 2H), 4.85 (s, 2H), 7.08 (d, *J*=8.6 Hz, 1H), 7.48 (dd, *J*=8.6, 2.3 Hz, 1H), 7.53 (d, *J*=2.3 Hz, 1H), 10.42 (s, 1H), 13.09 (br. s., 1H).

^{13}C NMR (201 MHz, DMSO-*d*$_6$) δ ppm: 15.5, 27.0, 65.3 (br. s.), 113.9, 124.4, 126.1, 135.6, 136.7, 158.6, 169.8 (br. s.), 189.2.

HRMS (ESI-TOF) found, m/z: 209.0807 $[M+H]^+$. $C_{11}H_{13}O_4^+$. Calculated, m/z: 209.0808.

2-(2-Formyl-4-isopropylphenoxy)acetic acid (5c)



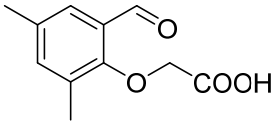
Yield 1.59 g (72%), white solid, m. p. 135-137 °C. R_f = 0.04.

^{1}H NMR (800 MHz, DMSO-*d*$_6$) δ ppm: 1.18 (d, *J*=6.9 Hz, 6H), 2.90 (spt, *J*=6.9 Hz, 1H), 4.85 (s, 2H), 7.08 (d, *J*=8.6 Hz, 1H), 7.53 (dd, *J*=8.6, 2.4 Hz, 1H), 7.56 (d, *J*=2.4 Hz, 1H), 10.42 (s, 1H), 13.10 (br. s., 1H).

^{13}C NMR (201 MHz, DMSO-*d*$_6$) δ ppm: 23.7, 32.4, 65.3, 113.9, 124.3, 124.6, 134.3, 141.2, 158.6, 169.9, 189.2.

HRMS (ESI-TOF) found, m/z: 223.0964 $[M+H]^+$. $C_{12}H_{15}O_4^+$. Calculated, m/z: 223.0965.

2-(2-Formyl-4,6-dimethylphenoxy)acetic acid (5d)



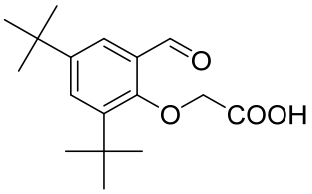
Yield 1.54 g (74%), white solid, m. p. 104-106 °C. R_f = 0.09.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 2.28 (s, 3H), 2.28 (s, 3H), 4.58 (s, 2H), 7.35 – 7.39 (m, 2H), 10.37 (s, 1H), 12.96 (br. s., 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 15.5, 20.0, 70.6, 125.7, 128.5, 131.5, 133.6, 138.2, 157.3, 170.1, 190.7.

HRMS (ESI-TOF) found, m/z: 209.0809 $[M+H]^+$. $C_{11}H_{13}O_4^+$. Calculated, m/z: 209.0808.

2-(2,4-Di-tert-butyl-6-formylphenoxy)acetic acid (5e)



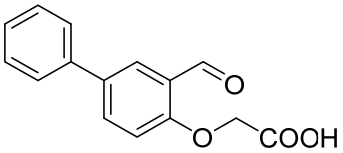
Yield 2.39 g (82%), yellowish solid, m. p. 141-143 °C. R_f = 0.18.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 1.30 (s, 9H), 1.39 (s, 9H), 4.54 (s, 2H), 7.64 (d, *J*=2.6 Hz, 1H), 7.67 (d, *J*=2.6 Hz, 1H), 10.18 (s, 1H), 12.99 (br. s., 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 30.5, 30.9, 34.3, 35.0, 73.2, 125.3, 128.8, 130.4, 142.6, 146.1, 157.3, 169.3, 190.7.

HRMS (ESI-TOF) found, m/z: 293.1750 $[M+H]^+$. $C_{17}H_{25}O_4^+$. Calculated, m/z: 293.1747.

2-((3-Formyl-[1,1'-biphenyl]-4-yl)oxy)acetic acid (5f)



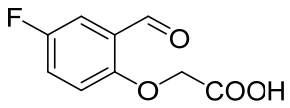
Yield 1.59 g (62%), white solid, m. p. 158-160 °C. R_f = 0.06.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 4.95 (s, 2H), 7.27 (d, *J*=8.5 Hz, 1H), 7.37 (t, *J*=7.3 Hz, 1H), 7.47 (t, *J*=7.6 Hz, 2H), 7.66 (d, *J*=7.5 Hz, 2H), 7.87 - 8.01 (m, 2H), 10.48 (s, 1H), 13.19 (br. s., 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 65.3, 114.6, 124.8, 125.4, 126.3, 127.4, 129.0, 133.3, 134.2, 138.6, 159.7, 169.8, 189.2.

HRMS (ESI-TOF) found, m/z: 257.0810 $[M+H]^+$. $C_{15}H_{13}O_4^+$. Calculated, m/z: 257.0808.

2-(4-Fluoro-2-formylphenoxy)acetic acid (5g)



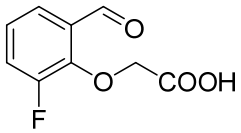
Yield 1.31 g (66%), white solid, m. p. 123-125 °C. R_f = 0.07.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 4.89 (s, 2H), 7.25 (dd, *J*=9.2, 4.0 Hz, 1H), 7.42 (dd, *J*=8.4, 3.3 Hz, 1H), 7.52 (td, *J*=8.6, 3.3 Hz, 1H), 10.39 (d, *J*=3.2 Hz, 1H), 13.14 (br. s., 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 65.8, 112.8 (d, *J*=23.4 Hz), 116.5 (d, *J*=7.6 Hz), 122.8 (d, *J*=23.8 Hz), 125.5 (d, *J*=4.2 Hz), 156.5 (d, *J*=239.6 Hz), 156.8 (d, *J*=1.4 Hz), 169.7, 188.4 (d, *J*=15.7 Hz).

HRMS (ESI-TOF) found, m/z: 199.0401 $[M+H]^+$. $C_9H_8FO_4^+$. Calculated, m/z: 199.0401.

2-(2-Fluoro-6-formylphenoxy)acetic acid (5h)



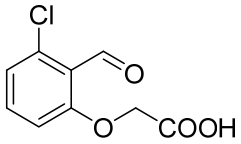
Yield 1.32 g (67%), white solid, m. p. 86-88 °C. R_f = 0.09.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 4.87 (s, 2H), 7.25 (td, *J*=7.9, 4.5 Hz, 1H), 7.55 (d, *J*=7.7 Hz, 1H), 7.61 (ddd, *J*=12.2, 8.1, 1.4 Hz, 1H), 10.46 (s, 1H), 13.12 (br. s., 1H)

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 69.6, 122.8, 122,9 (d, *J*=24.1 Hz), 124.2 (d, *J*=7.4 Hz), 130.0 (br. s.), 147.8 (d, *J*=10.3 Hz), 154.2 (d, *J*=247.0 Hz), 170.0, 189.2 (d, *J*=20.5 Hz).

HRMS (ESI-TOF) found, m/z: 199.0402 $[M+H]^+$. $C_9H_8FO_4^+$. Calculated, m/z: 199.0401.

2-(3-Chloro-2-formylphenoxy)acetic acid (5i)



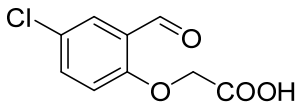
Yield 1.33 g (62%), white solid, m. p. 130-132 °C. R_f = 0.06.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 4.89 (s, 2H), 7.09 - 7.19 (m, 2H), 7.55 (t, *J*=8.3 Hz, 1H), 10.44 (s, 1H), 13.21 (br. s., 1H)

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 65.6, 112.8, 122.3, 123.5, 133.1, 135.1, 160.9, 169.5, 188.8.

HRMS (ESI-TOF) found, m/z: 215.0107 $[M+H]^+$. $C_9H_8ClO_4^+$. Calculated, m/z: 215.0106.

2-(4-Chloro-2-formylphenoxy)acetic acid (5j)



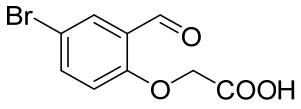
Yield 1.18 g (55%), white solid, m. p. 144-146 °C. R_f = 0.06.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 4.92 (s, 2H), 7.24 (d, *J*=9.0 Hz, 1H), 7.64 (d, *J*=2.5 Hz, 1H), 7.69 (dd, *J*=8.9, 2.6 Hz, 1H), 10.36 (s, 1H), 13.22 (br. s., 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 65.5, 116.4, 125.6, 125.7, 126.7, 135.4, 158.9, 169.5, 188.1.

HRMS (ESI-TOF) found, m/z: 215.0104 $[M+H]^+$. $C_9H_8ClO_4^+$. Calculated, m/z: 215.0106.

2-(4-Bromo-2-formylphenoxy)acetic acid (5k)



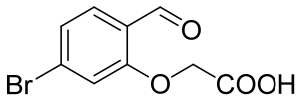
Yield 1.58 g (61%), yellowish solid, m. p. 164-166 °C. R_f = 0.05.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 4.91 (s, 2H), 7.18 (d, *J*=8.9 Hz, 1H), 7.76 (d, *J*=2.6 Hz, 1H), 7.80 (dd, *J*=8.9, 2.6 Hz, 1H), 10.34 (s, 1H), 13.19 (br. s., 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 65.4, 113.1, 116.8, 126.1, 129.7, 138.2, 159.3, 169.5, 188.1.

HRMS (ESI-TOF) found, m/z: 258.9599 $[M+H]^+$. $C_9H_8BrO_4^+$. Calculated, m/z: 258.9600.

2-(5-Bromo-2-formylphenoxy)acetic acid (5l)



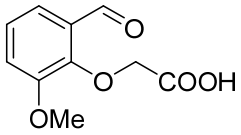
Yield 2.24 g (87%), yellowish solid, m. p. 160-162 °C. R_f = 0.09.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 4.96 (s, 2H), 7.32 (dd, *J*=8.2, 1.5 Hz, 1H), 7.47 (d, *J*=1.5 Hz, 1H), 7.63 (d, *J*=8.2 Hz, 1H), 10.36 (s, 1H), 13.20 (br. s., 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 65.5 (br. s.), 117.4, 123.7, 124.6, 129.2, 129.6, 160.5, 169.5 (br. s.), 188.4.

HRMS (ESI-TOF) found, m/z: 258.9599 $[M+H]^+$. $C_9H_8BrO_4^+$. Calculated, m/z: 258.9600.

2-(2-Formyl-6-methoxyphenoxy)acetic acid (5m)



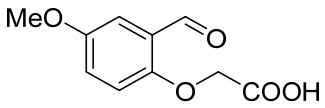
Yield 1.68 g (80%), white solid, m. p. 111-113 °C. R_f = 0.13.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 3.87 (s, 3H), 4.79 (s, 2H), 7.20 (t, *J*=7.9 Hz, 1H), 7.28 (dd, *J*=7.7, 1.1 Hz, 1H), 7.38 (d, *J*=8.2 Hz, 1H), 10.53 (s, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 56.1, 68.8 (br. s.), 117.9, 118.8, 124.3, 129.3, 149.7, 151.9, 170.6 (br. s.), 190.5.

HRMS (ESI-TOF) found, m/z: 211.0599 $[M+H]^+$. $C_{10}H_{11}O_5^+$. Calculated, m/z: 211.0601.

2-(2-Formyl-4-methoxyphenoxy)acetic acid (5o)



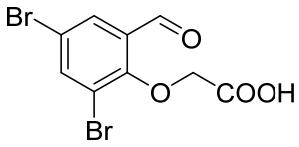
Yield 1.66 g (79%), white solid, m. p. 149-151 °C. R_f = 0.07.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 3.76 (s, 3H), 4.82 (s, 2H), 7.15 (d, *J*=9.1 Hz, 1H), 7.18 (d, *J*=3.2 Hz, 1H), 7.24 (dd, *J*=9.0, 3.3 Hz, 1H), 10.41 (s, 1H), 13.08 (br. s., 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 55.5, 65.9 (br. s.), 109.9, 116.0, 122.9, 125.1, 153.6, 154.8, 170.0 (br. s.), 189.0.

HRMS (ESI-TOF) found, m/z: 211.0599 $[M+H]^+$. $C_{10}H_{11}O_5^+$. Calculated, m/z: 211.0601.

2-(2,4-Dibromo-6-formylphenoxy)acetic acid (5p)



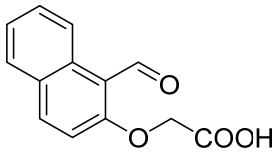
Yield 2.28 g (68%), yellowish solid, m. p. 168-170 °C. R_f = 0.08.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 4.79 (s, 2H), 7.82 (d, *J*=2.5 Hz, 1H), 8.23 (d, *J*=2.5 Hz, 1H), 10.33 (s, 1H), 13.16 (br. s., 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 70.1, 117.6, 118.4, 129.7, 132.1, 140.6, 156.6, 169.5, 188.4.

HRMS (ESI-TOF) found, m/z: 336.8709 $[M+H]^+$. $C_9H_7Br_2O_4^+$. Calculated, m/z: 336.8706.

2-((1-Formylnaphthalen-2-yl)oxy)acetic acid (5q)



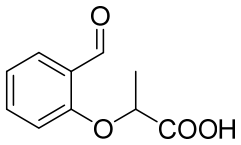
Yield 1.88 g (82%), white solid, m. p. 169-171 °C. R_f = 0.04.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 5.06 (s, 2H), 7.48 (ddd, *J*=8.0, 6.9, 1.1 Hz, 1H), 7.52 (d, *J*=9.2 Hz, 1H), 7.66 (ddd, *J*=8.5, 6.9, 1.3 Hz, 1H), 7.95 (d, *J*=8.0 Hz, 1H), 8.26 (d, *J*=9.2 Hz, 1H), 9.11 (d, *J*=8.6 Hz, 1H), 10.87 (s, 1H), 13.21 (br. s., 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 65.8, 114.6, 116.2, 123.9, 124.8, 128.4, 128.5, 129.7, 130.6, 137.6, 162.7, 169.8, 191.6.

HRMS (ESI-TOF) found, m/z: 231.0649 $[M+H]^+$. $C_{13}H_{11}O_4^+$. Calculated, m/z: 231.0652.

2-(2-Formylphenoxy)propanoic acid (5n)



A mixture of the 2-hydroxybenzaldehyde (1.22 g, 10 mmol), methyl 2-bromopropanoate (2.17 g, 13 mmol) and K_2CO_3 (2.76 g, 20 mmol) in freshly distilled DMF (50 mL) was heated at 80 °C for 4 h. EtOAc (200 mL) was added and the resulting mixture was washed with brine (3×50 mL). Organic layer was dried over anhydrous Na_2SO_4, all volatiles were removed in vacuo and the residue was dissolved in the mixture of 15 mL of THF, 5 mL of water and LiOH (720 mg, 30 mmol). The resulting mixture was stirred for 5 h and acidified with 5% aq. HCl to pH = 1. The resulted mixture was diluted with 200 mL of brine and extracted with CH_2Cl_2 (3×100 mL). Combined layers were washed with brine (10×30 mL) and dried over Na_2SO_4. All volatiles were removed in vacuo and the residue was purified with flash chromatography (Eluent – EtOAc. The R_f value presented below is given for this eluent. Short pad of silicagel was used, since the compound is very polar.).

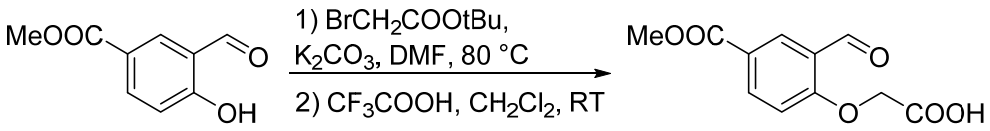
Yield 1.59 g (82%), yellowish solid, m. p. 67-69 °C. R_f = 0.13.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 1.59 (d, *J*=6.8 Hz, 3H), 5.08 (q, *J*=6.8 Hz, 1H), 7.08 - 7.13 (m, 2H), 7.60 - 7.65 (m, 1H), 7.70 (dd, *J*=7.6, 1.7 Hz, 1H), 10.45 (s, 1H), 13.16 (br. s., 1H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 18.1, 72.5, 114.4, 121.3, 124.8, 127.5, 136.1, 160.1, 172.6, 189.4.

HRMS (ESI-TOF) found, m/z: 195.0654 $[M+H]^+$. $C_{10}H_{11}O_4^+$. Calculated, m/z: 195.0652.

2-(2-Formyl-4-(methoxycarbonyl)phenoxy)acetic acid (5r)



A mixture of the methyl 3-formyl-4-hydroxybenzoate (1.80 g, 10 mmol), tert-butyl bromoacetate (2.54 g, 13 mmol) and K_2CO_3 (2.76 g, 20 mmol) in freshly distilled DMF (50 mL) was heated at 80 °C for 24 h. EtOAc (200 mL) was added and the resulting mixture was washed with brine (3×50 mL). Organic layer was dried over anhydrous Na_2SO_4, all volatiles were removed in vacuo and the residue was dissolved in the mixture of 5 mL of CF_3COOH and 5 mL of CH_2Cl_2. The resulting mixture was stirred for 1 h, diluted with 200 mL of brine and extracted with CH_2Cl_2 (3×100 mL). Combined layers were washed with brine (10×30 mL) and dried over Na_2SO_4. All volatiles were removed in vacuo and the residue was purified with flash chromatography (Eluent – EtOAc. The R_f value presented below is given for this eluent. Short pad of silicagel was used, since the compound is very polar.).

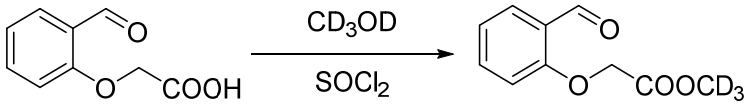
Yield 1.88 g (90%), white solid, m. p. 122-124 °C. R_f = 0.06.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 3.85 (s, 3H), 4.97 (s, 2H), 7.29 (d, *J*=8.8 Hz, 1H), 8.17 (dd, *J*=8.8, 2.3 Hz, 1H), 8.26 (d, *J*=2.3 Hz, 1H), 10.42 (s, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 52.2, 65.5, 114.3, 122.5, 124.2, 129.0, 136.5, 163.4, 165.1, 169.3, 188.5.

HRMS (ESI-TOF) found, m/z: 239.0551 $[M+H]^+$. $C_{11}H_{11}O_6^+$. Calculated, m/z: 239.0550.

4.3. Synthesis of methyl-d_3 2-(2-formylphenoxy)acetate (1a-d_3)



To the stirred solution of 2-(2-formylphenoxy)acetic acid **5a** (180 mg, 1 mmol) in CD_3OD (1.5 mL) $SOCl_2$ (143 mg, 1.2 mmol) was added dropwise. The resulting solution was stirred for 3 h, diluted with water (40 mL) and extracted with CH_2Cl_2 (3×30 mL). Combined organic layer was dried over anhydrous 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 20:1. The R_f value presented below is given for this eluent.).

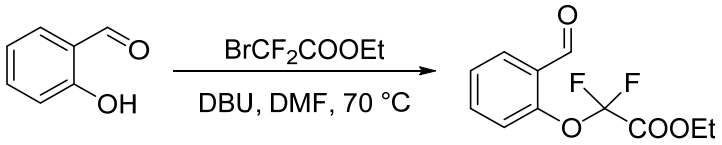
Yield 185 mg (94%), yellowish solid, m. p. 99-101 °C. $R_f = 0.16$.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 5.01 (s, 2H), 7.13 (t, *J*=7.4 Hz, 1H), 7.18 (d, *J*=8.4 Hz, 1H), 7.64 (ddd, *J*=8.6, 7.1, 1.9 Hz, 1H), 7.72 (dd, *J*=7.7, 1.8 Hz, 1H), 10.44 (s, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 51.1 (quin, *J*=22.6 Hz), 65.2, 113.9, 121.5, 124.6, 127.6, 136.1, 160.0, 168.8, 189.0.

HRMS (ESI-TOF) found, m/z: 198.0838 $[M+H]^+$. $C_{10}H_8D_3O_4^+$. Calculated, m/z: 198.0840.

4.4. Synthesis of ethyl 2,2-difluoro-2-(2-formylphenoxy)acetate (9a)



Mixture of 2-hydroxybenzaldehyde (1.22 g, 10 mmol), ethyl 2-bromo-2,2-difluoroacetate (5.07 g, 25 mmol) and DBU (3.8 g, 25 mmol) in freshly distilled DMF (50 mL) was heated at 70 °C overnight. EtOAc (200 mL) was added and the resulting mixture was washed with brine (3×50 mL). Organic layer was dried over anhydrous 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 20:1. The R_f value presented below is given for this eluent.).

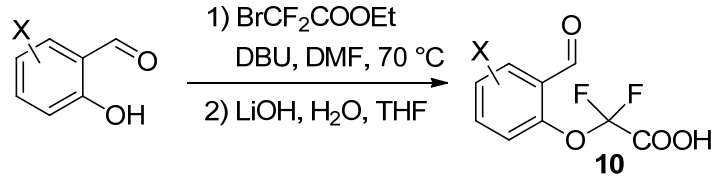
Yield 1.36 g (56%), yellowish viscous oil. R_f = 0.13.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 1.27 (t, *J*=7.1 Hz, 3H), 4.40 (q, *J*=7.1 Hz, 2H), 7.48 (d, *J*=8.8 Hz, 1H), 7.56 (t, *J*=7.5 Hz, 1H), 7.81 (ddd, *J*=8.2, 7.4, 1.8 Hz, 1H), 7.91 (dd, *J*=7.7, 1.7 Hz, 1H), 10.26 (s, 1H).

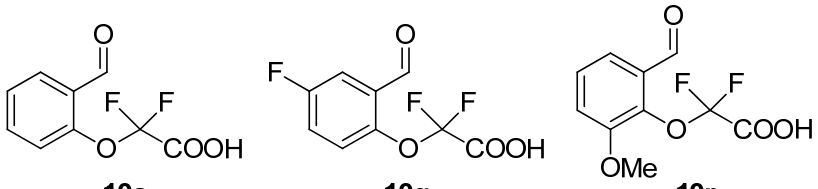
^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 13.5, 64.3, 113.5 (t, *J*=273.1 Hz), 122.6, 127.6, 128.6, 128.8, 136.1, 150.0, 158.4 (t, *J*=40.5 Hz), 188.3.

HRMS (ESI-TOF) found, m/z: 245.0623 $[M+H]^+$. $C_{11}H_{11}F_2O_4^+$. Calculated, m/z: 245.0620.

4.5. Synthesis of ethyl 2,2-difluoro-2-(2-formylphenoxy) acetic acids (10)



10

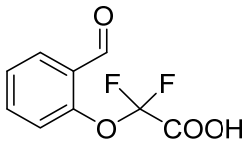


10a **10g** **10r**

General method

Mixture of the corresponding 2-hydroxybenzaldehyde (10 mmol), ethyl 2-bromo-2,2-difluoroacetate (5.07 g, 25 mmol) and DBU (3.8 g, 25 mmol) in freshly distilled DMF (50 mL) was heated at 70 °C overnight. EtOAc (200 mL) was added and the resulting mixture was washed with brine (3×50 mL). Organic layer was dried over anhydrous Na_2SO_4, all volatiles were removed in vacuo. The residue was dissolved in the mixture of THF (40 mL) and water (8 mL) and then LiOH (720 mg, 30 mmol) was added. The resulting mixture was stirred for 4 h and 5% HCl was added dropwise to pH = 1. Water (200 mL) was added and the resulting solution was extracted with CH_2Cl_2 (3×100 mL). Combined organic layers were dried over anhydrous Na_2SO_4, all volatiles were removed in vacuo and the residue was purified with flash chromatography (Eluent – mixture of toluene and EtOAc, v/v 1:1. The R_f values presented below are given for this eluent. Short pads of silicagel were used, since the compounds are very polar.).

2,2-Difluoro-2-(2-formylphenoxy)acetic acid (10a)



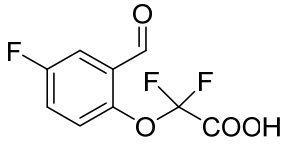
Yield 0.95 g (44%), brown solid, m. p. 120-122 °C. R_f = 0.09.

^{1}H NMR (800 MHz, DMSO-*d*$_6$) δ ppm: 7.45 (d, *J*=8.2 Hz, 1H), 7.52 (t, *J*=7.5 Hz, 1H), 7.79 (ddd, *J*=8.2, 7.4, 1.8 Hz, 1H), 7.88 (dd, *J*=7.7, 1.7 Hz, 1H), 10.28 (s, 1H).

13C NMR (201 MHz, DMSO-*d*$_6$) δ ppm: 114.3 (t, *J*=274.3 Hz), 122.5, 127.2, 128.5, 128.7, 136.1, 150.9, 160.3 (t, *J*=38.5 Hz), 188.4.

HRMS (ESI-TOF) found, m/z: 217.0308 $[M+H]^+$. $C_9H_7F_2O_4^+$. Calculated, m/z: 217.0307.

2,2-Difluoro-2-(4-fluoro-2-formylphenoxy)acetic acid (10g)



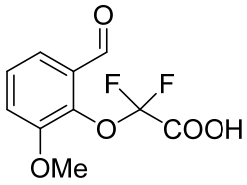
Yield 0.96 g (41%), brown solid, m. p. 70-72 °C. R_f = 0.04.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 7.52 (dd, *J*=9.0, 4.2 Hz, 1H), 7.62 (dd, *J*=8.2, 3.3 Hz, 1H), 7.66 (ddd, *J*=9.0, 8.0, 3.3 Hz, 1H), 10.20 (d, *J*=2.8 Hz, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 114.1 (t, *J*=274.8 Hz), 114.3 (d, *J*=24.2 Hz), 122.8 (d, *J*=24.2 Hz), 125.3 (d, *J*=8.3 Hz), 130.5 (d, *J*=6.7 Hz), 146.7 (d, *J*=1.9 Hz), 160.02 (d, *J*=246.4 Hz), 160.04 (t, *J*=38.1 Hz), 187.5.

HRMS (ESI-TOF) found, m/z: 235.0216 $[M+H]^+$. $C_9H_6F_3O_4^+$. Calculated, m/z: 235.0213.

2,2-Difluoro-2-(2-formyl-6-methoxyphenoxy)acetic acid (10m)



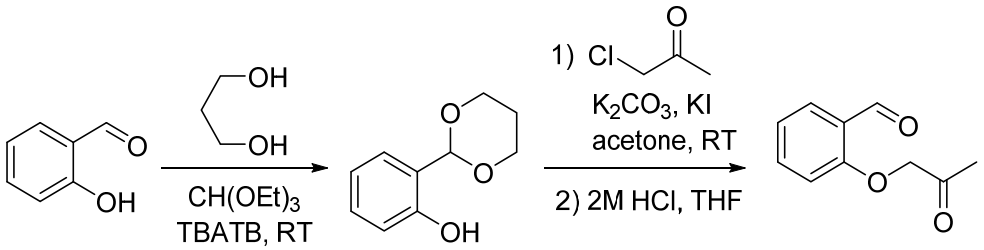
Yield 0.89 g (36%), off-white solid, m. p. 93-95 °C. R_f = 0.05.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 3.86 (s, 3H), 7.40 (dd, *J*=7.7, 1.5 Hz, 1H), 7.47 (t, *J*=8.0 Hz, 1H), 7.53 (dd, *J*=8.2, 1.4 Hz, 1H), 10.21 (s, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 56.5, 114.2 (t, *J*=275.3 Hz), 118.8, 119.3, 128.1, 130.9, 139.5, 152.8, 160.3 (t, *J*=39.3 Hz), 188.7.

HRMS (ESI-TOF) found, m/z: 247.0415 $[M+H]^+$. $C_{10}H_9F_2O_5^+$. Calculated, m/z: 247.0413.

4.6. Synthesis of 2-(2-oxopropoxy)benzaldehyde (13)



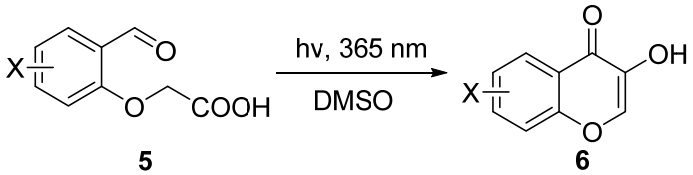
Mixture of 2-hydroxybenzaldehyde (1.22 g, 10 mmol), 1,3-propanediol (1.52 g, 20 mmol), triethyl orthoformate (1.63 g, 11 mmol) and tetrabutylammonium tetrabromide (48 mg, 0.1 mmol) was stirred overnight. Brine (100 mL) was added and the resulting mixture was extracted with EtOAc (3×100 mL). Combined organic layers was dried over anhydrous Na_2SO_4, all volatiles were removed in vacuo. The residue was dissolved in acetone (60 mL) and then chloroacetone (1.11 g, 12 mmol), K_2CO_3 (2.76 g, 20 mmol) and KI (1.99 g, 12 mmol) were added. The resulting mixture was refluxed for 8 h and all volatiles were removed in vacuo. Brine (100 mL) was added and the resulted mixture was extracted with EtOAc (3×100 mL). Combined organic layers was dried over anhydrous Na_2SO_4, all volatiles were removed in vacuo. The residue was dissolved in the mixture of THF (24 mL) and 2M HCl (10 mL) and the resulted solution was stirred for 8 h. Saturated aqueous solution of $NaHCO_3$ (100 mL) was carefully added and the resulted mixture was extracted with EtOAc (3×100 mL). Combined organic layers was dried over anhydrous Na_2SO_4, all volatiles were removed in vacuo. The residue was purified with flash chromatography (eluent – mixture of hexane and EtOAc, v/v 10:1). Yield 0.99 g (56%).

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm 2.20 (s, 3H), 5.01 (s, 2H), 7.06 - 7.12 (m, 2H), 7.56 - 7.65 (m, 1H), 7.71 (dd, J=7.9, 1.7 Hz, 1H), 10.46 (s, 1H).

The spectral properties corresponded to the literature data.[5]

5. Photochemical scaled experiments

5.1. Photocyclisation of 2-(2-formylphenoxy)acetic acids 5



5 **6**

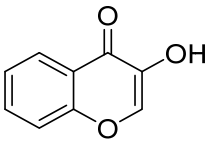
General method

Corresponding 2-(2-formylphenoxy)acetic acid **5** (1.0 mmol) was dissolved in freshly distilled 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 ^{1}H NMR. After the reaction completion, reaction mixtures were dissolved in 200 mL of EtOAc, washed with saturated KCl solution[1] (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. The R_f values presented below are given for this eluent.).

3-Hydroxy-4*H*-chromen-4-one (6a)



Yield 103 mg (64%), white solid, m. p. 168-170 °C. R_f = 0.19.

Reaction time ~ 15 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 7.45 (t, *J*=7.5 Hz, 1H), 7.63 (d, *J*=8.4 Hz, 1H), 7.74 - 7.78 (m, 1H), 8.12 (dd, *J*=8.0, 1.3 Hz, 1H), 8.23 (s, 1H), 9.11 (s, 1H).

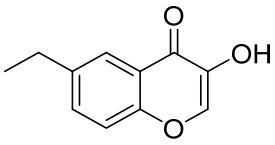
^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 118.4, 122.7, 124.5, 124.9, 133.3, 140.7, 141.8, 155.3, 172.7.

The spectral properties corresponded to the literature data.[6]

HRMS (ESI-TOF) found, m/z: 163.0390 $[M+H]^+$. $C_9H_7O_3^+$. Calculated, m/z: 163.0390.

[1] From our experience, saturated KCl solution removes DMSO from organic solvents more effectively than a solution of sodium chloride.

6-Ethyl-3-hydroxy-4*H*-chromen-4-one (6b)



Yield 98 mg (52%), white solid, m. p. 115-117 °C. R_f = 0.25.

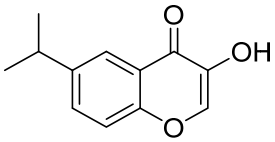
Reaction time ~ 15 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 1.23 (t, *J*=7.6 Hz, 3H), 2.74 (q, *J*=7.6 Hz, 2H), 7.55 (d, *J*=8.7 Hz, 1H), 7.62 (dd, *J*=8.6, 2.2 Hz, 1H), 7.91 (d, *J*=1.8 Hz, 1H), 8.20 (s, 1H), 9.05 (s, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 15.4, 27.4, 118.3, 122.5, 122.7, 133.5, 140.1, 140.6, 141.7, 153.8, 172.6.

HRMS (ESI-TOF) found, m/z: 191.0705 $[M+H]^+$. $C_{11}H_{11}O_3^+$. Calculated, m/z: 191.0703.

3-Hydroxy-6-isopropyl-4*H*-chromen-4-one (6c)



Yield 96 mg (47%), white solid, m. p. 139-141 °C. R_f = 0.27.

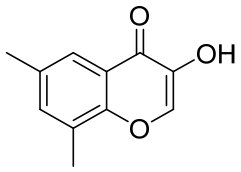
Reaction time ~ 20 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 1.25 (d, *J*=6.9 Hz, 6H), 3.06 (spt, *J*=6.8 Hz, 1H), 7.56 (d, *J*=8.7 Hz, 1H), 7.68 (dd, *J*=8.7, 2.2 Hz, 1H), 7.92 (d, *J*=2.2 Hz, 1H), 8.20 (s, 1H), 9.05 (s, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 23.7, 32.8, 118.4, 121.2, 122.4, 132.2, 140.6, 141.7, 144.7, 153.8, 172.7.

HRMS (ESI-TOF) found, m/z: 205.0860 $[M+H]^+$. $C_{12}H_{13}O_3^+$. Calculated, m/z: 205.0859.

3-Hydroxy-6,8-dimethyl-4*H*-chromen-4-one (6d)



Yield 101 mg (53%), white solid, m. p. 170-172 °C. R_f = 0.23.

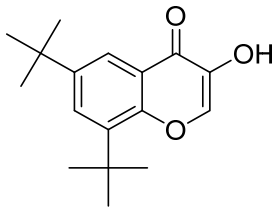
Reaction time ~ 15 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 2.38 (s, 3H), 2.41 (s, 3H), 7.45 (s, 1H), 7.73 (s, 1H), 8.24 (s, 1H), 9.01 (s, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 15.0, 20.3, 121.7, 122.3, 127.1, 133.4, 135.1, 140.4, 141.6, 152.2, 172.7.

HRMS (ESI-TOF) found, m/z: 191.0705 $[M+H]^+$. $C_{11}H_{11}O_3^+$. Calculated, m/z: 191.0703.

6,8-Di-tert-butyl-3-hydroxy-4*H*-chromen-4-one (6e)



Yield 85 mg (31%), yellowish solid, m. p. 143-145 °C. R_f = 0.37.

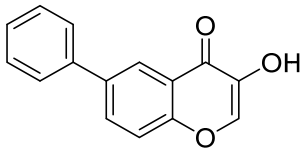
Reaction time ~ 7 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 1.35 (s, 9H), 1.46 (s, 9H), 7.67 (d, J=2.5 Hz, 1H), 7.95 (d, J=2.4 Hz, 1H), 8.29 (s, 1H), 9.03 (s, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 29.6, 31.0, 34.5, 34.8, 118.3, 122.9, 127.6, 138.4, 139.8, 141.4, 146.0, 152.4, 172.9.

HRMS (ESI-TOF) found, m/z: 275.1644 $[M+H]^+$. $C_{17}H_{23}O_3^+$. Calculated, m/z: 275.1642.

3-Hydroxy-6-phenyl-4*H*-chromen-4-one (6f)



Yield 50 mg (21%), yellowish solid, m. p. 91-93 °C. R_f = 0.14.

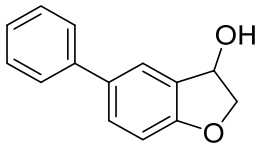
Reaction time ~ 7 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 7.42 (t, *J*=7.3 Hz, 1H), 7.52 (t, *J*=7.7 Hz, 2H), 7.74 (d, *J*=8.7 Hz, 1H), 7.75 - 7.77 (m, 2H), 8.08 (dd, *J*=8.7, 2.4 Hz, 1H), 8.27 (s, 1H), 8.30 (d, *J*=2.3 Hz, 1H), 9.19 (s, 1H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 70.1, 79.1, 110.0, 124.0, 126.2, 126.5, 128.3, 128.8, 130.7, 132.9, 140.3, 159.5.

HRMS (ESI-TOF) found, m/z: 239.0705 $[M+H]^+$. $C_{15}H_{11}O_3^+$. Calculated, m/z: 239.0703.

5-Phenyl-2,3-dihydrobenzofuran-3-ol (8f)



Yield 89 mg (42%), colorless viscous oil. R_f = 0.17.

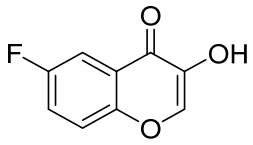
Reaction time ~ 7 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 4.28 (dd, *J*=9.9, 3.1 Hz, 1H), 4.56 (dd, *J*=9.9, 6.9 Hz, 1H), 5.33 (td, *J*=6.1, 3.2 Hz, 1H), 5.63 (d, *J*=5.6 Hz, 1H), 6.91 (d, *J*=8.3 Hz, 1H), 7.31 (t, *J*=7.4 Hz, 1H), 7.43 (t, *J*=7.7 Hz, 2H), 7.51 (dd, *J*=8.3, 2.0 Hz, 1H), 7.59 (d, *J*=7.2 Hz, 2H), 7.64 (d, *J*=1.9 Hz, 1H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 70.6, 79.6, 110.5, 124.6, 126.7, 127.1, 128.8, 129.3, 131.2, 133.4, 140.8, 160.0.

HRMS (ESI-TOF) found, m/z: 213.0911 $[M+H]^+$. $C_{14}H_{13}O_2^+$. Calculated, m/z: 213.0910.

6-Fluoro-3-hydroxy-4*H*-chromen-4-one (6g)



Yield 95 mg (53%), white solid, m. p. 191-193 °C. R_f = 0.18.

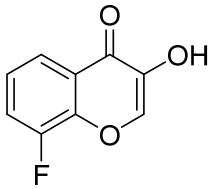
Reaction time ~ 6 h.

^{1}H NMR (800 MHz, DMSO-*d*$_6$) δ ppm: 7.64 - 7.69 (m, 1H), 7.74 (dd, *J*=9.2, 4.3 Hz, 1H), 7.77 (dd, *J*=8.5, 3.1 Hz, 1H), 8.27 (s, 1H), 9.23 (s, 1H).

^{13}C NMR (201 MHz, DMSO-*d*$_6$) δ ppm: 109.1 (d, *J*=23.7 Hz), 121.2 (d, *J*=8.5 Hz), 121.7 (d, *J*=25.8 Hz), 123.7 (d, *J*=7.4 Hz), 141.2, 141.5, 151.8, 158.4 (d, *J*=243.4 Hz), 172.0 (d, *J*=2.2 Hz).

HRMS (ESI-TOF) found, m/z: 181.0298 $[M+H]^+$. $C_9H_6FO_3^+$. Calculated, m/z: 181.0295.

8-Fluoro-3-hydroxy-4*H*-chromen-4-one (6h)



Yield 121 mg (68%), white solid, m. p. 187-189 °C. R_f = 0.16.

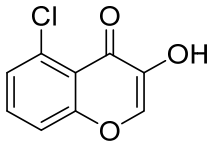
Reaction time ~ 15 h.

^{1}H NMR (800 MHz, DMSO-*d*$_6$) δ ppm: 7.43 (td, *J*=8.0, 4.6 Hz, 1H), 7.72 (dd, *J*=10.5, 8.4 Hz, 1H), 7.91 (d, *J*=8.1 Hz, 1H), 8.31 (s, 1H), 9.33 (s, 1H).

^{13}C NMR (201 MHz, DMSO-*d*$_6$) δ ppm: 118.7 (d, *J*=16.3 Hz), 120.4 (d, *J*=3.8 Hz), 124.4 (d, *J*=6.8 Hz), 124.8, 140.6, 142.2, 143.9 (d, *J*=11.8 Hz), 150.7 (d, *J*=250.5 Hz), 172.0 (d, *J*=2.3 Hz).

HRMS (ESI-TOF) found, m/z: 181.0293 $[M+H]^+$. $C_9H_6FO_3^+$. Calculated, m/z: 181.0295.

5-Chloro-3-hydroxy-4*H*-chromen-4-one (6i)



Yield 53 mg (27%), white solid, m. p. 160-162 °C. R_f = 0.23.

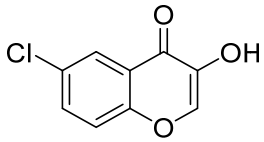
Reaction time ~ 7 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 7.46 (dd, *J*=7.7, 0.9 Hz, 1H), 7.59 (dd, *J*=8.5, 0.9 Hz, 1H), 7.67 (t, *J*=8.1 Hz, 1H), 8.20 (s, 1H), 9.07 (s, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 118.1, 119.3, 127.0, 131.5, 132.9, 138.9, 142.4, 156.9, 171.7.

HRMS (ESI-TOF) found, m/z: 197.0003 $[M+H]^+$. $C_9H_6ClO_3^+$. Calculated, m/z: 197.0000.

6-Chloro-3-hydroxy-4*H*-chromen-4-one (6j)



Yield 92 mg (47%), white solid, m. p. 198-200 °C. R_f = 0.21.

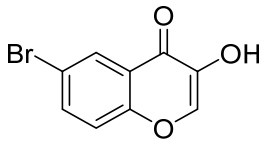
Reaction time ~ 7 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 7.71 (d, *J*=8.9 Hz, 1H), 7.80 (dd, *J*=9.0, 2.6 Hz, 1H), 8.04 (d, *J*=2.6 Hz, 1H), 8.27 (s, 1H), 9.31 (s, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 120.9, 123.7, 123.8, 129.0, 133.2, 141.2, 141.9, 153.8, 171.6.

HRMS (ESI-TOF) found, m/z: 197.0001 $[M+H]^+$. $C_9H_6ClO_3^+$. Calculated, m/z: 197.0000.

6-Bromo-3-hydroxy-4*H*-chromen-4-one (6k)



Yield 134 mg (56%), yellowish solid, m. p. 143-145 °C. R_f = 0.22.

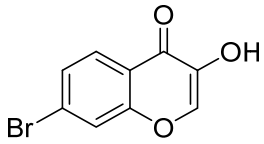
Reaction time ~ 6 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 7.64 (d, *J*=8.9 Hz, 1H), 7.91 (dd, *J*=9.0, 2.5 Hz, 1H), 8.18 (d, *J*=2.5 Hz, 1H), 8.27 (s, 1H), 9.31 (s, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 116.9, 121.1, 124.3, 126.9, 135.9, 141.2, 142.0, 154.1, 171.5.

HRMS (ESI-TOF) found, m/z: 240.9496 $[M+H]^+$. $C_9H_6BrO_3^+$. Calculated, m/z: 240.9495.

7-Bromo-3-hydroxy-4*H*-chromen-4-one (6l)



Yield 152 mg (63%), yellowish solid, m. p. 174-176 °C. R_f = 0.19.

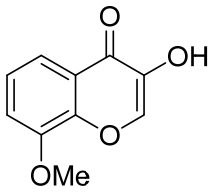
Reaction time ~ 7 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 7.62 (dd, *J*=8.6, 1.7 Hz, 1H), 7.98 (d, *J*=1.7 Hz, 1H), 8.02 (d, *J*=8.6 Hz, 1H), 8.23 (s, 1H), 9.26 (s, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 121.1, 121.8, 126.5, 126.8, 127.8, 140.8, 142.1, 155.4, 172.2.

HRMS (ESI-TOF) found, m/z: 240.9498 $[M+H]^+$. $C_9H_6BrO_3^+$. Calculated, m/z: 240.9495.

3-Hydroxy-8-methoxy-4*H*-chromen-4-one (6m)



Yield 84 mg (44%), white solid, m. p. 166-168 °C. R_f = 0.11.

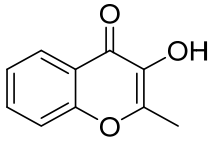
Reaction time ~ 12 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 3.94 (s, 3H), 7.34 - 7.38 (m, 2H), 7.63 (dd, *J*=7.2, 2.2 Hz, 1H), 8.25 (s, 1H), 9.13 (s, 1H).

^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 56.0, 113.9, 115.3, 123.6, 124.1, 140.2, 141.7, 145.7, 148.6, 172.3.

HRMS (ESI-TOF) found, m/z: 193.0493 $[M+H]^+$. $C_{10}H_9O_4^+$. Calculated, m/z: 193.0495.

3-Hydroxy-2-methyl-4*H*-chromen-4-one (6n)



Yield 96 mg (55%), white solid, m. p. 176-178 °C. R_f = 0.28.

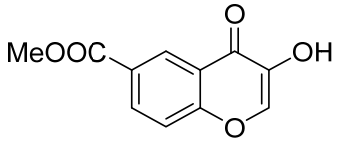
Reaction time ~ 15 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 2.40 (s, 3H), 7.38 - 7.46 (m, 1H), 7.59 (d, *J*=8.4 Hz, 1H), 7.73 (ddd, *J*=8.5, 7.0, 1.6 Hz, 1H), 8.07 (dd, *J*=8.0, 1.5 Hz, 1H), 8.81 (s, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 14.8, 118.0, 122.1, 124.3, 124.8, 133.0, 138.3, 150.2, 154.5, 171.5.

HRMS (ESI-TOF) found, m/z: 177.0548 $[M+H]^+$. $C_{10}H_9O_3^+$. Calculated, m/z: 177.0546.

Methyl 3-hydroxy-4-oxo-4*H*-chromene-6-carboxylate (6r)



Yield 147 mg (67%), white solid, m. p. 145-147 °C. R_f = 0.18.

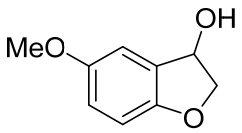
Reaction time ~ 7 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 3.91 (s, 3H), 7.76 (d, *J*=8.8 Hz, 1H), 8.24 (dd, *J*=8.8, 2.1 Hz, 1H), 8.29 (s, 1H), 8.68 (d, *J*=2.1 Hz, 1H), 9.40 (s, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 52.4, 119.4, 122.4, 125.7, 127.0, 133.0, 141.1, 142.2, 157.6, 165.1, 172.4.

HRMS (ESI-TOF) found, m/z: 221.0442 $[M+H]^+$. $C_{11}H_9O_5^+$. Calculated, m/z: 221.0444.

5-Methoxy-2,3-dihydrobenzofuran-3-ol (8o)



Yield 74 mg (45%), yellowish viscous oil. $R_f = 0.44$.

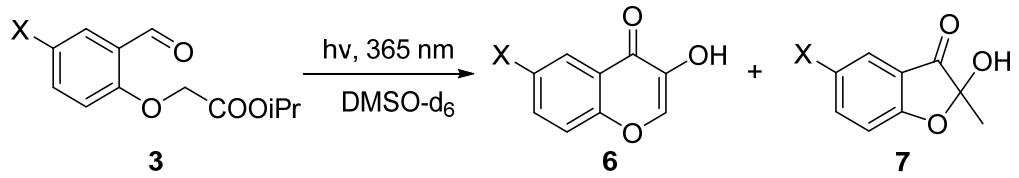
Reaction time ~ 7 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 3.70 (s, 3H), 4.18 (dd, *J*=9.9, 3.3 Hz, 1H), 4.46 (dd, *J*=9.9, 7.0 Hz, 1H), 5.23 (td, *J*=6.1, 3.5 Hz, 1H), 5.55 (d, *J*=5.6 Hz, 1H), 6.72 (d, *J*=8.6 Hz, 1H), 6.78 (dd, *J*=8.6, 2.7 Hz, 1H), 6.93 (d, *J*=2.6 Hz, 1H)

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 56.1, 71.1, 79.2, 110.3, 111.4, 115.9, 131.0, 154.1, 154.2.

HRMS (ESI-TOF) found, m/z: 167.0702 $[M+H]^+$. $C_9H_{11}O_3^+$. Calculated, m/z: 167.0703.

5.2. 2-Hydroxy-2-methylbenzofuran-3(2H)-ones 7



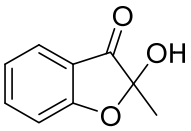
3 **6** **7**

General method

Corresponding isopropyl 2-(2-formylphenoxy)acetate **3** (1.0 mmol) was dissolved in freshly distilled 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 progress of the reaction was monitored by TLC and ^{1}H NMR. After the reaction completion, reaction mixtures were dissolved in 200 mL of EtOAc, washed with saturated KCl solution[2] (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. The R_f values presented below are given for this eluent.).

2-Hydroxy-2-methylbenzofuran-3(2H)-one (7a)



Yield 62 mg (38%) from **3a**, white solid, m. p. 72-74 °C. R_f = 0.28.

Reaction time ~ 15 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 1.45 (s, 3H), 7.12 (t, *J*=7.4 Hz, 1H), 7.14 (d, *J*=8.3 Hz, 1H), 7.62 (dd, *J*=7.6, 0.8 Hz, 1H), 7.68 (s, 1H), 7.71 - 7.75 (m, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 21.7, 104.1, 113.2, 118.5, 121.7, 124.6, 139.0, 169.4, 199.2.

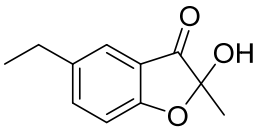
The spectral properties corresponded to the literature data.[7]

HRMS (ESI-TOF) found, m/z: 165.0544 $[M+H]^+$. $C_9H_9O_3^+$. Calculated, m/z: 165.0546.

Additionally, 3-hydroxy-4*H*-chromen-4-one (**6a**) was isolated from this reaction mixture, yield 48 mg (30%). ^{1}H, ^{13}C and HRMS data are presented above.

[2] From our experience, saturated KCl solution removes DMSO from organic solvents more effectively than a solution of sodium chloride.

5-Ethyl-2-hydroxy-2-methylbenzofuran-3(2*H*)-one (7b)



Yield 74 mg (39%) from **3b**, colorless viscous oil. R_f = 0.22.

Reaction time ~ 30 h.

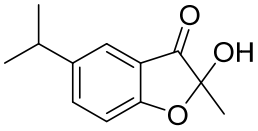
^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 1.17 (t, *J*=7.6 Hz, 3H), 1.44 (s, 3H), 2.61 (q, *J*=7.6 Hz, 2H), 7.06 (d, *J*=8.4 Hz, 1H), 7.43 (d, *J*=1.3 Hz, 1H), 7.59 (dd, *J*=8.4, 1.7 Hz, 1H), 7.62 (br. s., 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 21.7, 23.8, 32.6, 104.3, 113.0, 118.3, 121.1, 137.9, 142.1, 168.0, 199.3.

HRMS (ESI-TOF) found, m/z: 193.0857 $[M+H]^+$. $C_{11}H_{13}O_3^+$. Calculated, m/z: 193.0859.

Additionally, 6-ethyl-3-hydroxy-4*H*-chromen-4-one (**6b**) was isolated from this reaction mixture, yield 53 mg (28%). ^{1}H, ^{13}C and HRMS data are presented above.

2-Hydroxy-5-isopropyl-2-methylbenzofuran-3(2*H*)-one (7c)



Yield 73 mg (35%) from **3c**, colorless viscous oil. R_f = 0.20.

Reaction time ~ 30 h.

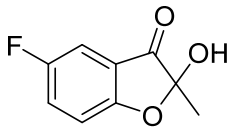
^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 1.20 (d, *J*=6.9 Hz, 6H), 1.44 (s, 3H), 2.93 (spt, *J*=6.9 Hz, 1H), 7.07 (d, *J*=8.5 Hz, 1H), 7.45 (d, *J*=1.7 Hz, 1H), 7.61 (s, 1H), 7.64 (dd, *J*=8.5, 1.8 Hz, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 15.7, 21.7, 27.2, 104.3, 113.0, 118.4, 122.7, 137.5, 139.1, 168.0, 199.2.

HRMS (ESI-TOF) found, m/z: 207.1017 $[M+H]^+$. $C_{12}H_{15}O_3^+$. Calculated, m/z: 207.1016.

Additionally, 3-hydroxy-6-isopropyl-4*H*-chromen-4-one (**6c**) was isolated from this reaction mixture, yield 65 mg (32%). ^{1}H, ^{13}C and HRMS data are presented above.

5-Fluoro-2-hydroxy-2-methylbenzofuran-3(2*H*)-one (7g)



Yield 62 mg (34%) from **3g**, white solid, m. p. 50-52 °C. R_f = 0.18.

Reaction time ~ 12 h.

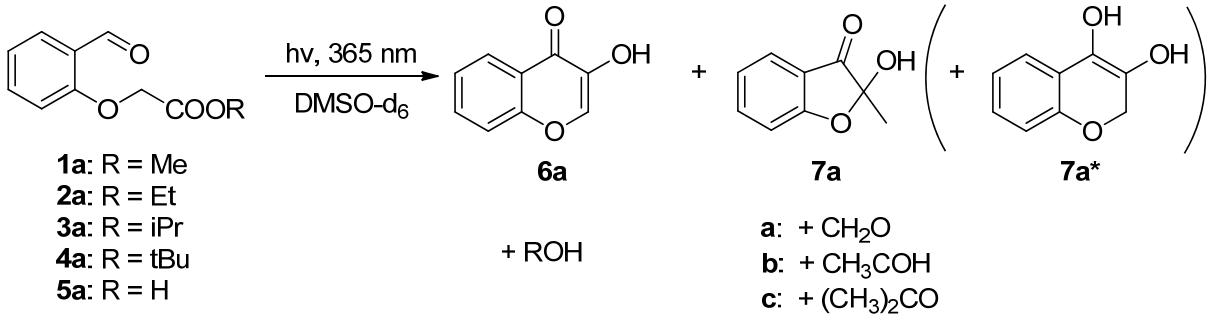
^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 1.47 (s, 3H), 7.20 (dd, *J*=9.0, 3.7 Hz, 1H), 7.47 (dd, *J*=7.0, 2.9 Hz, 1H), 7.63 (td, *J*=9.0, 2.9 Hz, 1H), 7.82 (br. s., 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 21.7, 45.6, 109.8 (d, *J*=23.5 Hz), 114.9 (d, *J*=7.7 Hz), 118.9 (d, *J*=7.8 Hz), 126.5 (d, *J*=25.7 Hz), 156.9 (d, *J*=240.0 Hz), 165.8, 199.1 (d, *J*=2.6 Hz).

HRMS (ESI-TOF) found, m/z: 183.0444 $[M+H]^+$. $C_9H_8FO_3^+$. Calculated, m/z: 183.0452.

Additionally, 6-fluoro-3-hydroxy-4*H*-chromen-4-one (**6g**) was isolated from this reaction mixture, yield 74 mg (41%). ^{1}H, ^{13}C and HRMS data are presented above.

6. Kinetic study



Compound **1a-5a** (0.05 mmol) was 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) were transferred to two argon-filled 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 ^{1}H NMR. One of the two samples was wrapped in a foil and served as a blank standard confirming that the reaction does not proceed without irradiation at similar conditions (solvent, time, temperature) (Figure S5-9). TMS signal was used as an internal standard - for all spectra its integral area was set on equal value. Initial integral area of aldehyde singlet signal from 10.25 ppm to 10.75 ppm was used as 100%. The conversion of components was determined using the following integral areas:

- singlet from 10.25 ppm to 10.75 ppm (1H) for the starting aldehyde **3a**.
- doublet of doublets signal from 8.04 ppm to 8.16 ppm (1H) for product **6a**
- singlet from 1.37 ppm to 1.54 ppm (3H) for product **7a**
- doublet of doublets signal from 6.63 ppm to 6.70 ppm (1H) for product **7a***
- septet signal from 3.69 ppm to 3.82 ppm (1H) for iPrOH
- singlet from 2.00 ppm to 2.12 ppm (6H) for acetone

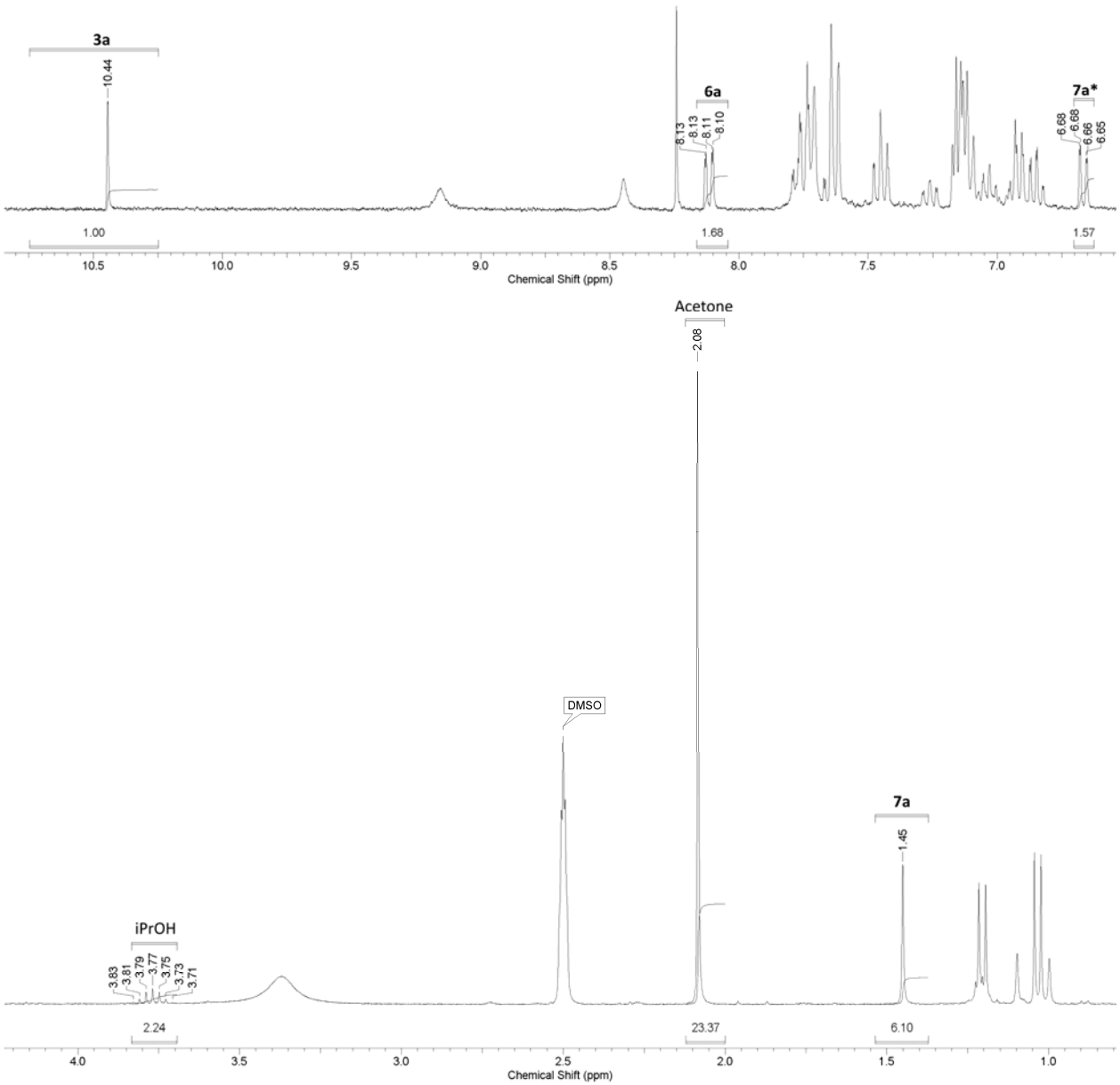


Figure S4. Example of ^{1}H NMR after one hour of **3a** irradiation.

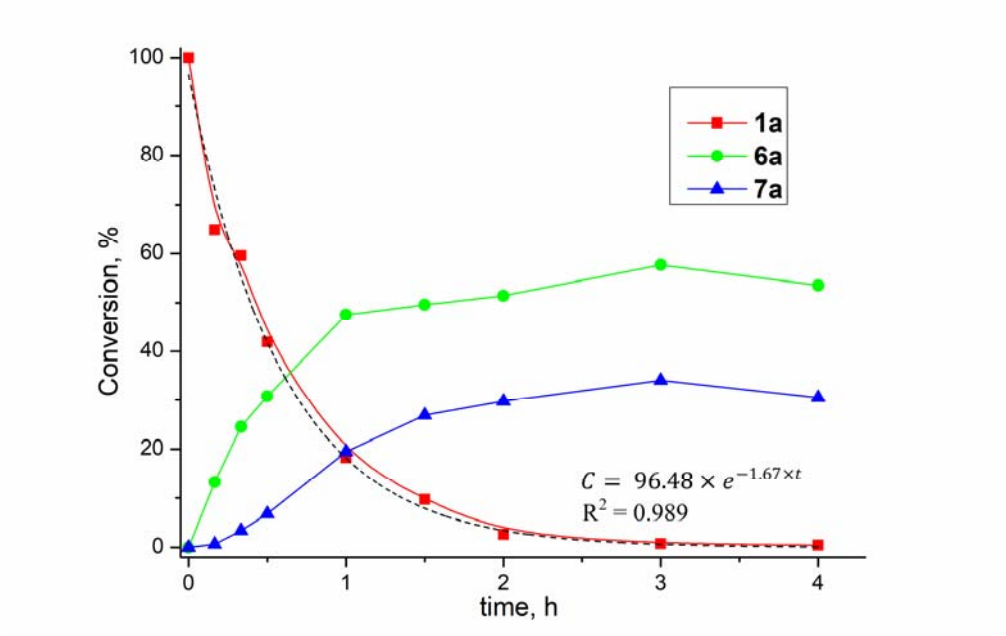


Figure S5. Kinetic study of compound **1a**.

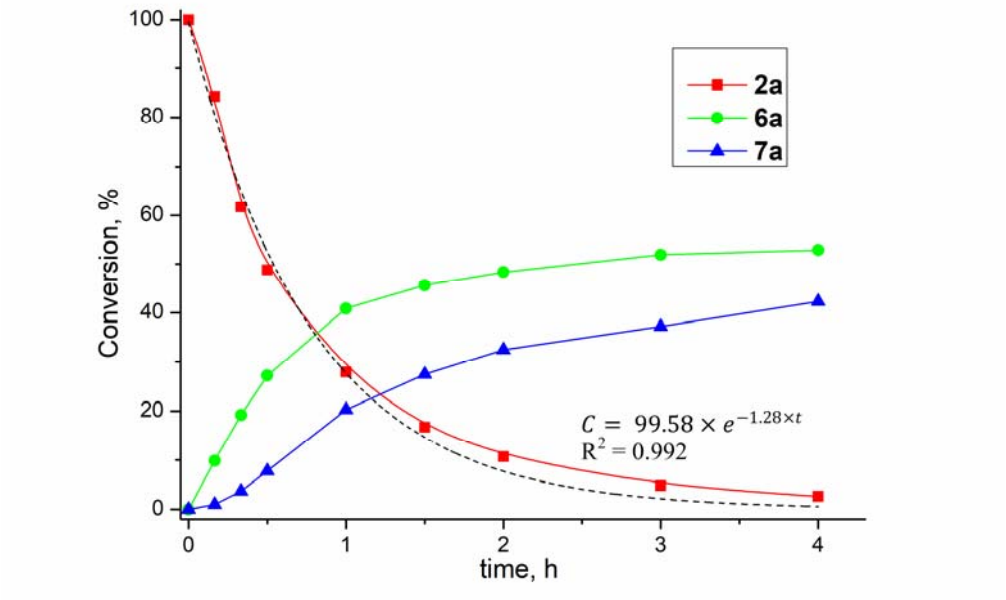


Figure S6. Kinetic study of compound **2a**.

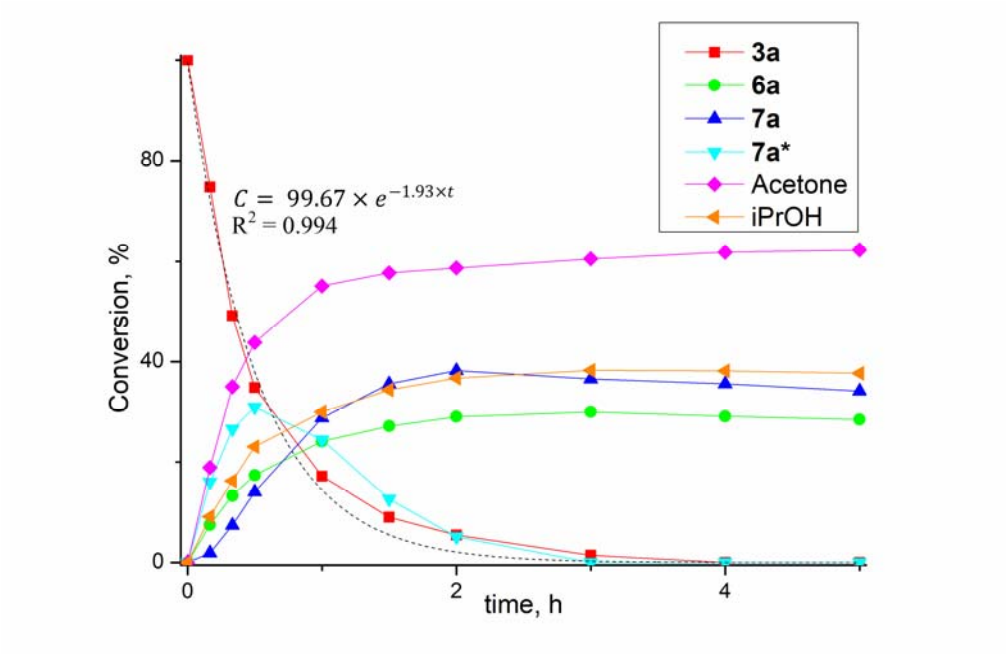


Figure S7. Kinetic study of compound **3a**.

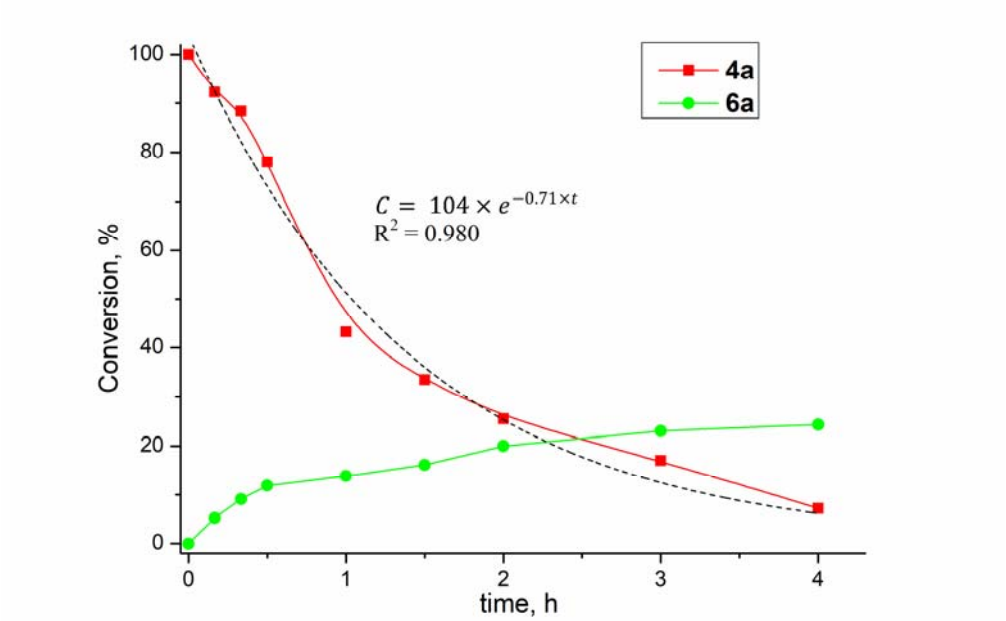


Figure S8. Kinetic study of compound **4a**.

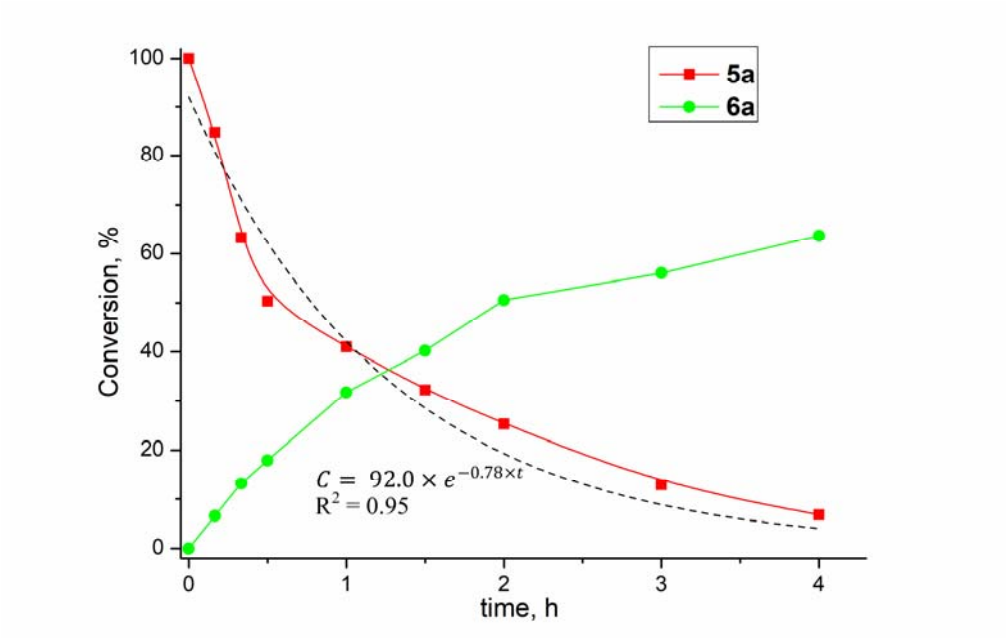
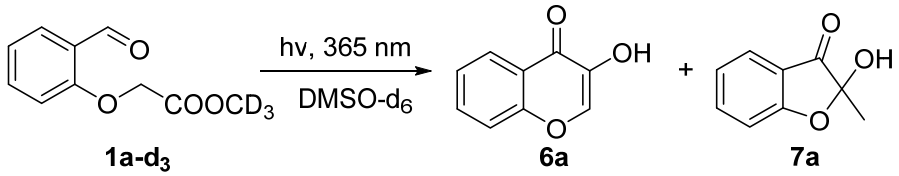


Figure S9. Kinetic study of compound **5a**.

7. Experiments with deuterated starting substance 1a-d_3

7.1. Kinetic study



1a-d_3 **6a** **7a**

Compound **1a-d_3** (5 mg, 0.025 mmol) was 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. Another NMR tube with **1a** solution in DMSO-*d*$_6$ was prepared in the same way. NMR tubes with these solutions were irradiated with 365 nm LED lamp in Evoluchem™ PhotoRedOx box. The mixtures were analyzed by ^{1}H NMR (see above in Part 6).

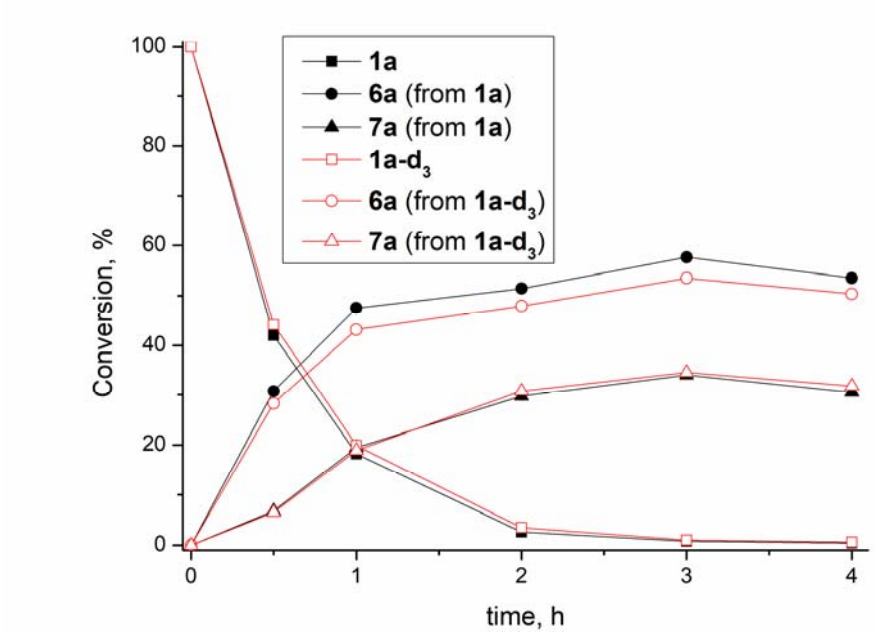
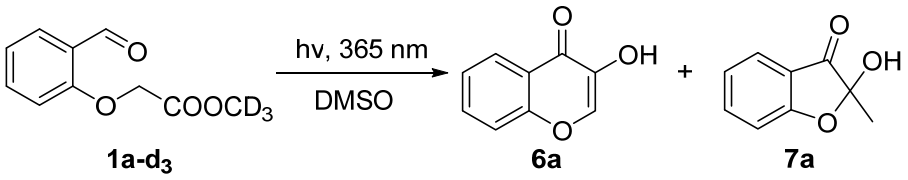


Figure S10. Kinetic study of **1a** phototranformation in comparison with deuterated compound **1a-d_3**.

7.2. Large scale experiment with 1a-d_3

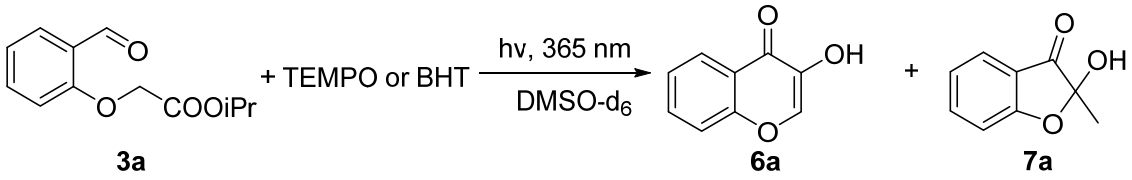


1a-d_3 **6a** **7a**

Compound **1a-d_3** (194 mg, 1.0 mmol) was dissolved in freshly distilled 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 progress of the reaction was monitored by TLC and ^{1}H NMR. After 15 h no starting compound was observed and the reaction mixture was 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). Yield of **6a** 77 mg (48%), yield of **7a** 45 mg (28%). ^{1}H, ^{13}C and HRMS data are presented above in Part 5.

8. Experiments with radical quenching reagents

8.1. Isopropyl 2-(2-formylphenoxy)acetate 3a.



3a **6a** **7a**

Compound **3a** (27 mg, 0.12 mmol) was dissolved in 4 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 four argon-filled NMR tubes and sealed. (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO, 3 mg, 0.02 mmol) was added to two tubes, butylated hydroxytoluene (BHT, 4 mg, 0.02 mmol) was added to the third, and the last tube was used without additives. NMR tubes with these solutions were sealed and irradiated with 365 nm LED lamp in Evoluchem™ PhotoRedOx box. One NMR tube with additional TEMPO was stored in the dark at similar conditions (time, temperature); no products were observed. The mixtures were analyzed by ^{1}H NMR (see above in Part 6).

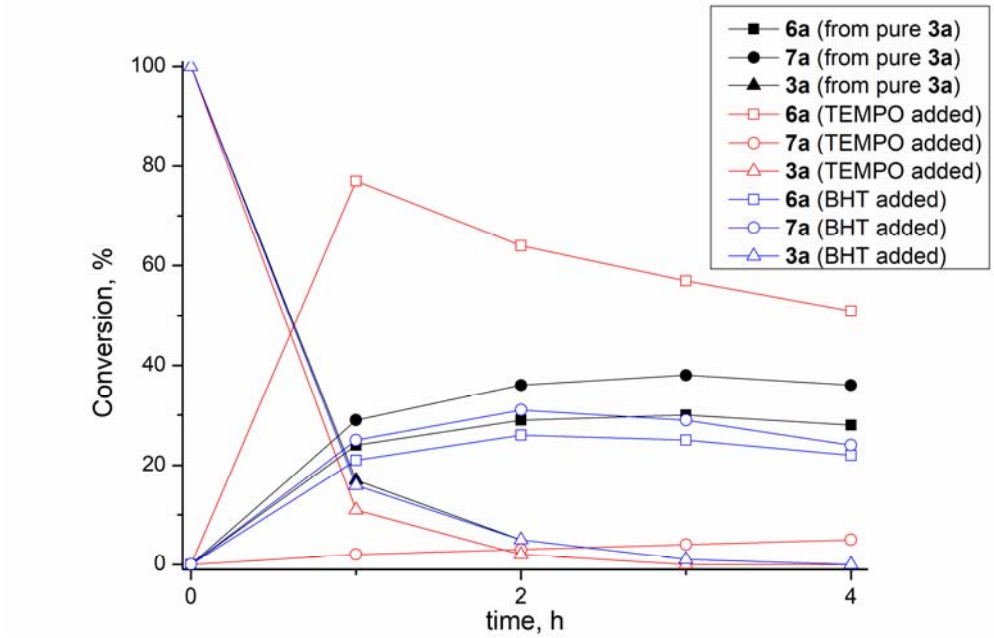
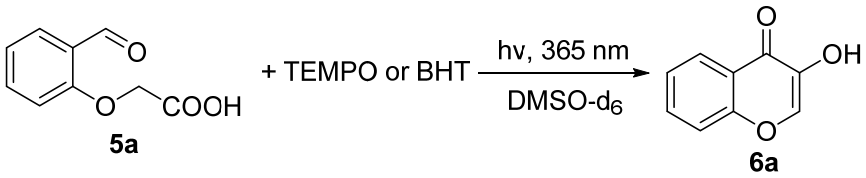


Figure S11. Kinetic study of **3a** phototranformation with BHT and TEMPO.

8.2. 2-(2-Formylphenoxy)acetic acid 5a



Compound **5a** (16 mg, 0.09 mmol) was dissolved in 3 mL of DMSO-d_6 in a Schlenk vessel. Next, parts of the solution (0.65 mL) were transferred to four argon-filled NMR tubes and sealed. TEMPO (3 mg, 0.02 mmol) was added to two tubes, BHT (4 mg, 0.02 mmol) was added to the third, and the last tube was used without additives. NMR tubes with these solutions were sealed and irradiated with 365 nm LED lamp in Evoluchem™ PhotoRedOx box. One NMR tube with additional TEMPO was stored in the dark at similar conditions (time, temperature); no products were observed. The mixtures were analyzed by ^{1}H NMR (see above in Part 6).

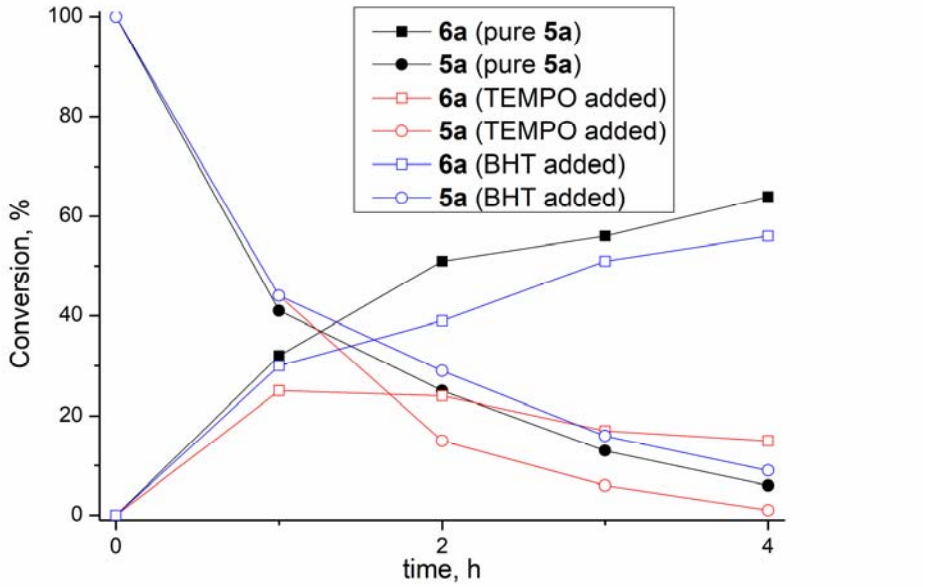


Figure S12. Kinetic study of **5a** phototranformation with BHT and TEMPO.

9. Experiments with increased concentration of 3a and 4-anisaldehyde addition

Compound **3a** (25 mg, 0.11 mmol) was 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, 0.65 mL of the solution were transferred to an argon-filled NMR tube and sealed. Another portion of **3a** (10 mg, 0.04 mmol) was treated the similar way for preparation of two equal NMR samples. 4-Anisaldehyde (3 mg, 0.02 mmol) was added to one of these tubes. All three NMR tubes with these solutions were irradiated with 365 nm LED lamp in Evoluchem™ PhotoRedOx box. The mixtures were analyzed by ^{1}H NMR (see above in Part 6).

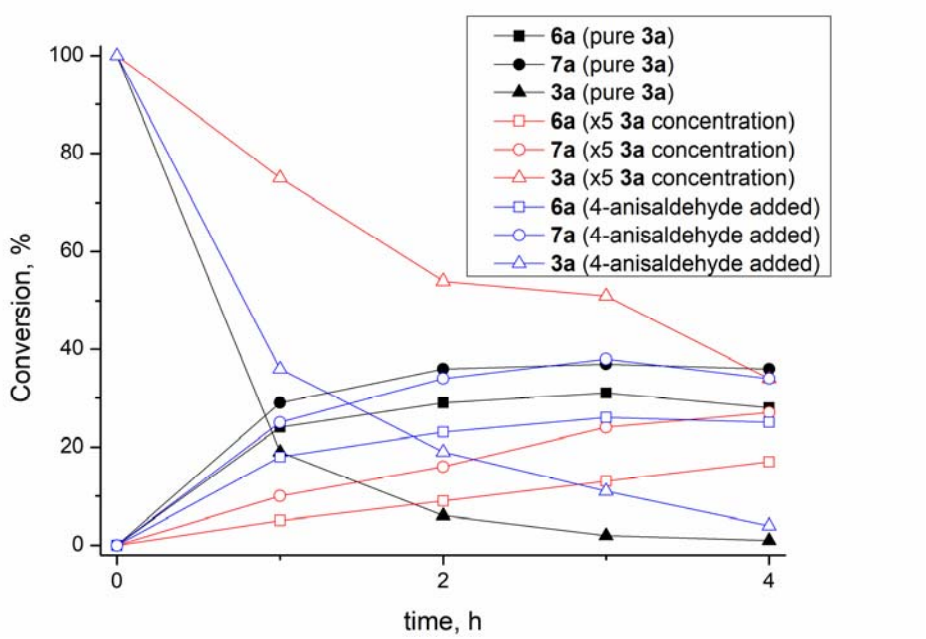


Figure S13. Kinetic study of **3a** phototranformation with increased concentration and additional 4-anisaldehyde.

10. Experiment with additional MeOH

Compound **5a** (10 mg, 0.06 mmol) was 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) were transferred to two argon-filled NMR tubes and sealed. Methanol (0.06 mmol, 3 eq.) was added to one tube. NMR tubes with these solutions were sealed and irradiated with 365 nm LED lamp in Evoluchem™ PhotoRedOx box. The mixtures were analyzed by ^{1}H NMR (see above in Part 6). No **7a** was observed.

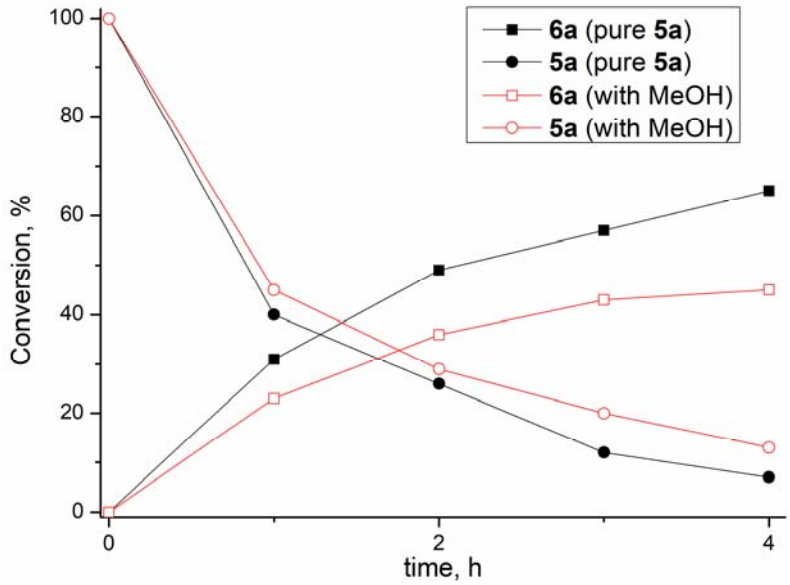
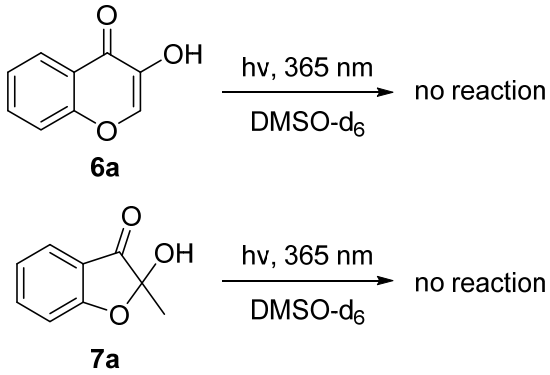


Figure S14. Kinetic study of **3a** phototranformation with MeOH addition.

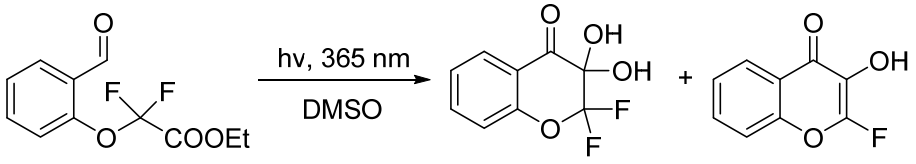
11. Photoexperiments with 6a and 7a



Compound **6a-7a** (5 mg, 0.03 mmol) was 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, parts of the solution (0.65 mL) were transferred to argon-filled NMR tubes and sealed. NMR tubes with these solutions of **6a** and **7a** were irradiated with 365 nm LED lamp in Evoluchem™ PhotoRedOx box for 6 h. The mixtures were analyzed by ^{1}H NMR (see above in Part 6). No reactions were observed.

12. Experiments with related compounds

12.1. Photocyclisation of ethyl 2,2-difluoro-2-(2-formylphenoxy)acetate (9a)



9a **11a** **12a**

Compound **9a** (244 mg, 1.0 mmol) was dissolved in freshly distilled 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 progress of the reaction was monitored by TLC and ^{1}H NMR. After 6 h no starting compound was observed and the reaction mixture was dissolved in 200 mL of EtOAc, washed with saturated KCl solution[3] (10×30 mL) and dried over Na_2SO_4. All volatiles were removed in vacuo and the mixture was weighted and analyzed by NMR.

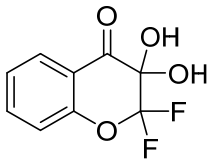
The yields of components were determined using the following integral areas:

- doublet of doublets signal from 8.06 ppm to 8.13 ppm (1H) for product **12a**
- singlet from 7.96 ppm to 8.06 ppm (2H) for product **11a**

Next, Et_2O was added (5 mL) and the mixture was filtered. Precipitate was washed additionally by Et_2O (2×5 mL) giving pure compound **12a** that was dried in vacuo. Yield 34 mg (19%). The Et_2O solution was evaporated in vacuo and the residue was purified with flash chromatography (Eluent – mixture of hexane and EtOAc, v/v 5:1. The R_f value presented below is given for this eluent.) to obtain pure **11a**. Yield 65 mg (30%). Compound **12a** was extremely unstable under silica column conditions, which resulted in yield decrease in comparison with initial mixture analysis.

[3] From our experience, saturated KCl solution removes DMSO from organic solvents more effectively than a solution of sodium chloride.

2,2-Difluoro-3,3-dihydroxychroman-4-one (11a)



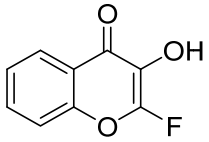
Yield 65 mg (30%) off-white solid, m. p. 113-115 °C. R_f = 0.09.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 7.30 (dd, *J*=8.3, 0.5 Hz, 1H), 7.32 - 7.38 (m, 1H), 7.73 - 7.81 (m, 1H), 7.89 (dd, *J*=7.8, 1.6 Hz, 1H), 7.99 (s, 2H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 89.1 (t, *J*=31.1 Hz), 117.7, 117.9, 122.4 (t, *J*=269.8 Hz), 124.7, 127.7, 137.6, 153.7, 188.2.

HRMS (ESI-TOF) found, m/z: 199.0199 $[M–H_2O+H]^+$. $C_9H_5F_2O_3^+$. Calculated, m/z: 199.0201.

2-Fluoro-3-hydroxy-4*H*-chromen-4-one (12a)



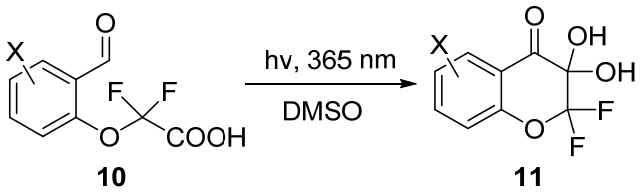
Yield 34 mg (19%) off-white solid, m. p. 220 °C with decomposition.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 7.53 (t, J=7.5 Hz, 1H), 7.70 (d, J=8.3 Hz, 1H), 7.80 - 7.84 (m, 1H), 8.10 (dd, J=8.0, 1.5 Hz, 1H), 9.37 (s, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 117.8, 121.8, 122.0 (d, J=7.1 Hz), 125.0 - 125.2 (m), 125.6, 133.9, 150.3 (d, J=2.6 Hz), 155.5 (d, J=271.2 Hz), 174.9 (d, J=11.5 Hz).

HRMS (ESI-TOF) found, m/z: 181.0294 $[M+H]^+$. $C_9H_6FO_3^+$. Calculated, m/z: 181.0295.

12.2. Photocyclisation of 2,2-difluoro-2-(2-formylphenoxy)acetic acids 10



10 **11**

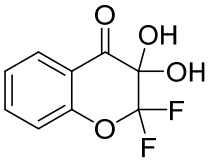
General method

Corresponding 2,2-difluoro-2-(2-formylphenoxy)acetic acid **10** (1.0 mmol) was dissolved in freshly distilled 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 ^{1}H NMR. After the reaction completion, reaction mixtures were dissolved in 200 mL of EtOAc, washed with saturated KCl solution[4] (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. The R_f values presented below are given for this eluent.).

2,2-Difluoro-3,3-dihydroxychroman-4-one (11a)



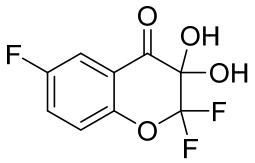
Yield 196 mg (91%).

Reaction time ~ 6 h.

^{1}H, ^{13}C and HRMS data are presented above in Part 12.1.

[4] From our experience, saturated KCl solution removes DMSO from organic solvents more effectively than a solution of sodium chloride.

2,2,6-Trifluoro-3,3-dihydroxychroman-4-one (11g)



Yield 201 mg (86%), dark solid, m. p. 74-76 °C. R_f = 0.10.

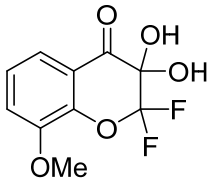
Reaction time ~ 6 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 7.40 (dd, *J*=9.0, 4.1 Hz, 1H), 7.64 (dd, *J*=7.8, 3.1 Hz, 1H), 7.68 (td, *J*=8.5, 3.1 Hz, 1H), 8.10 (s, 2H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 89.0 (t, *J*=31.2 Hz), 112.9 (d, *J*=24.3 Hz), 118.9 (d, *J*=6.7 Hz), 120.1 (d, *J*=7.9 Hz), 122.3 (t, *J*=270.3 Hz), 124.8 (d, *J*=24.5 Hz), 149.9 (d, *J*=1.2 Hz), 157.7, 158.9, 187.5.

HRMS (ESI-TOF) found, m/z: 235.0213 $[M+H]^+$. $C_9H_6F_3O_4^+$. Calculated, m/z: 235.0213.

2,2-Difluoro-3,3-dihydroxy-8-methoxychroman-4-one (11m)



Yield 157 mg (64%), yellowish solid, m. p. 120-122 °C. R_f = 0.04.

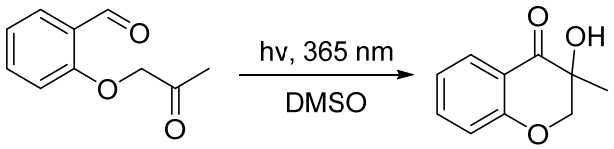
Reaction time ~ 6 h.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 3.88 (s, 3H), 7.27 (t, *J*=8.0 Hz, 1H), 7.41 (dd, *J*=7.8, 1.2 Hz, 1H), 7.47 (dd, *J*=8.1, 0.9 Hz, 1H), 7.97 (s, 2H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 56.3, 89.0 (t, *J*=31.1 Hz), 118.0, 118.5, 119.6, 122.6 (t, *J*=270.0 Hz), 124.6, 143.2 (br. s.), 148.0, 188.4.

HRMS (ESI-TOF) found, m/z: 229.0309 $[M–H_2O+H]^+$. $C_{10}H_7F_2O_4^+$. Calculated, m/z: 229.0307.

12.3. Photocyclisation of 2-(2-oxopropoxy)benzaldehyde (13)



13 **14**

2-(2-Oxopropoxy)benzaldehyde **13** (178 mg, 1.0 mmol) was dissolved in freshly distilled DMSO (20 mL) in a Schlenk vessel. The mixtures were degassed under vacuum and filled with argon three times. Obtained solution was irradiated with 365 nm LED lamp in Evoluchem™ PhotoRedOx box with stirring. After 6 hours, no starting component **9** was observed in the reaction mixture by TLC and ^{1}H NMR. The reaction mixture was dissolved in 200 mL of EtOAc, washed with saturated KCl solution[5] (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. The R_f value presented below is given for this eluent.).

Yield 94 mg (53%), white solid, m. p. 145-147 °C. R_f = 0.22.

^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 1.26 (s, 3H), 4.17 - 4.29 (m, 2H), 5.83 (s, 1H), 7.03 (d, *J*=8.3 Hz, 1H), 7.06 - 7.12 (m, 1H), 7.57 (ddd, *J*=8.5, 7.0, 1.7 Hz, 1H), 7.78 (dd, *J*=7.8, 1.6 Hz, 1H).

^{13}C NMR (201 MHz, DMSO-d_6) δ ppm: 20.2, 69.6, 74.8, 117.6, 119.0, 121.4, 127.1, 135.9, 160.6, 193.5.

HRMS (ESI-TOF) found, m/z: 179.0703 $[M+H]^+$. $C_{10}H_{11}O_3^+$. Calculated, m/z: 179.0703.

[5] From our experience, saturated KCl solution removes DMSO from organic solvents more effectively than a solution of sodium chloride.

12. References

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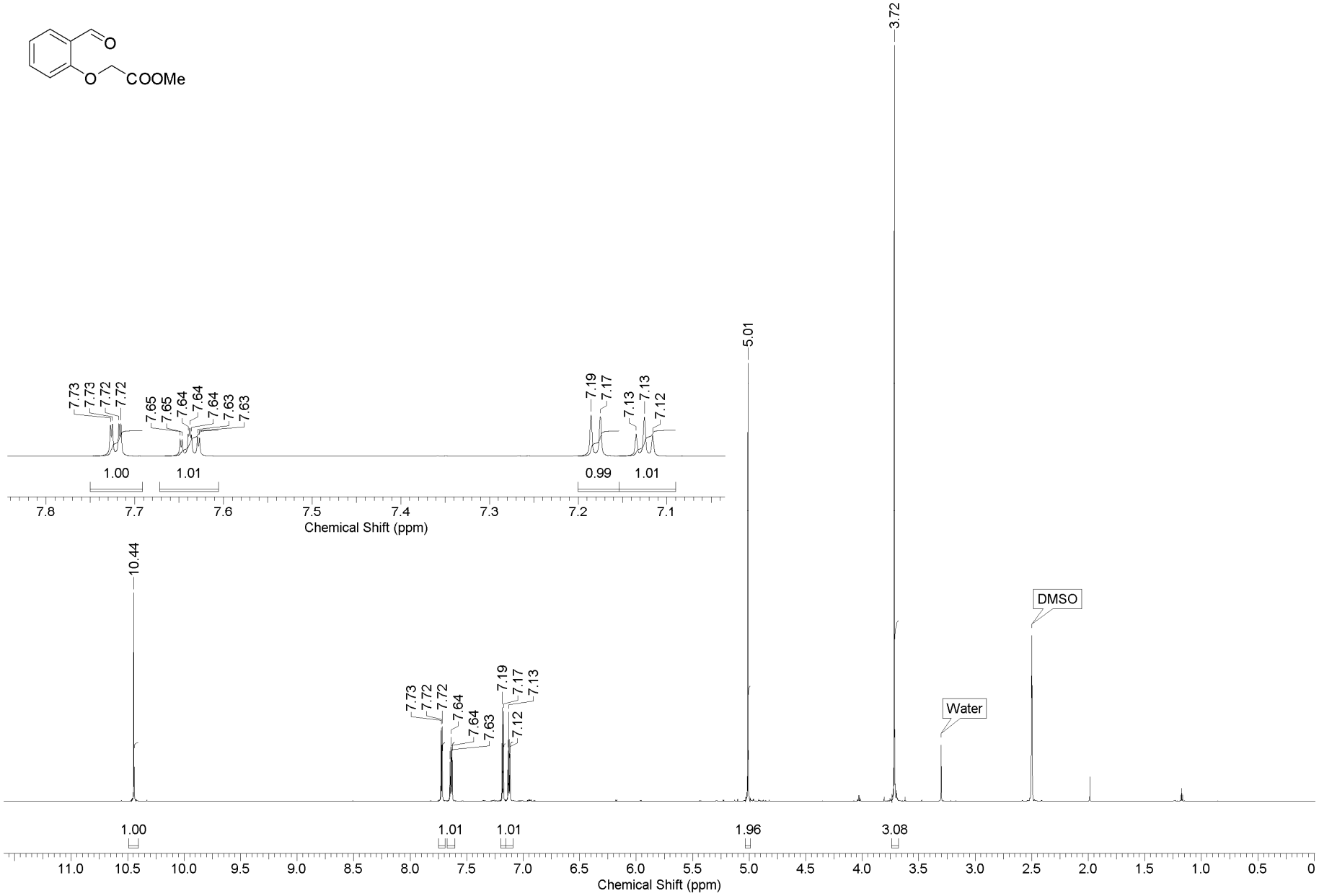
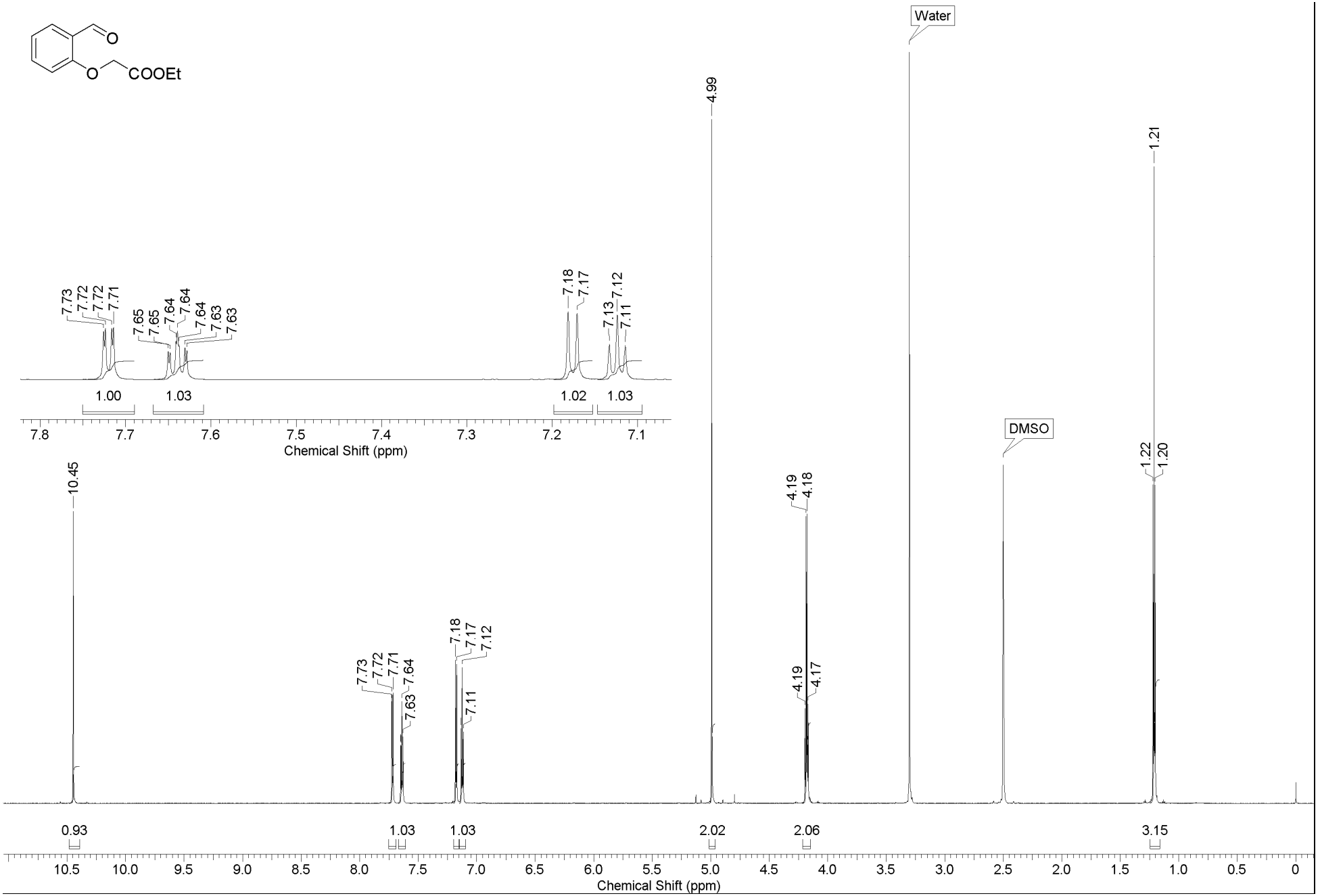
[6] Gudipati, R.; Kandula, V.; Raghavulu, K.; Basavaiah, K.; Yennam, S.; Behera, M., *ChemistrySelect* **2020**, *5*, 7093–7097.

[7] Fan, R.; Sun, Y.; Ye, Y., *Org. Lett.* **2009**, *11*, 5174–5177.

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




O
O
COOEt
Water
DMSO
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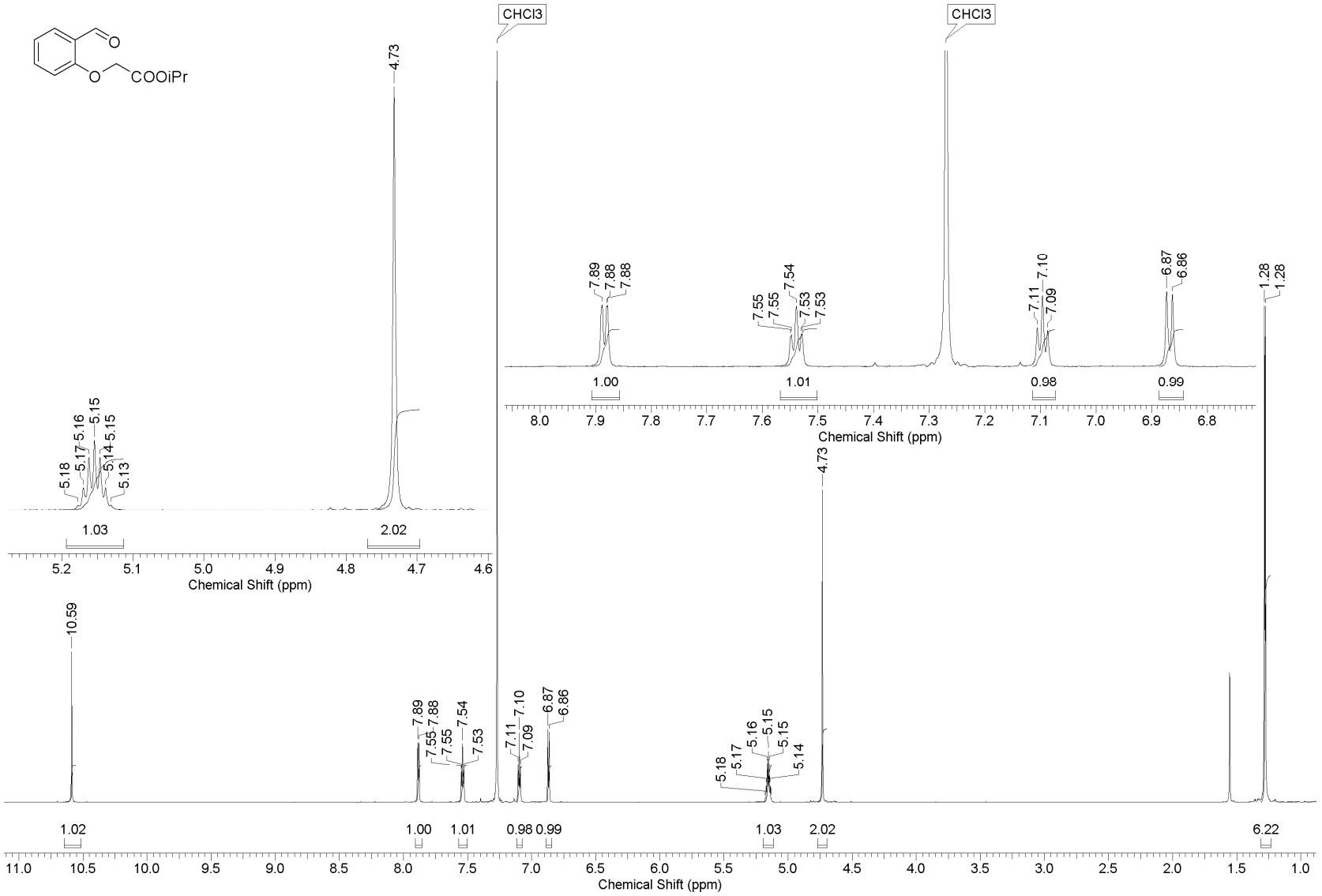
1.21
1.22
1.20
10.45
4.19
4.18
4.17
7.73
7.72
7.71
7.64
7.63
7.18
7.17
7.12
7.11
7.65
7.65
7.64
7.64
7.63
7.63
7.13
0.93
1.03
1.03
2.02
2.06
3.15
1.00
1.03
1.02
1.03
Chemical Shift (ppm)
Chemical Shift (ppm)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7.88
7.55
7.55
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7.53
7.11
7.10
7.09
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6.86
1.28
1.28
5.18
5.17
5.16
5.15
5.15
5.14
5.13
1.03
2.02
1.00
1.01
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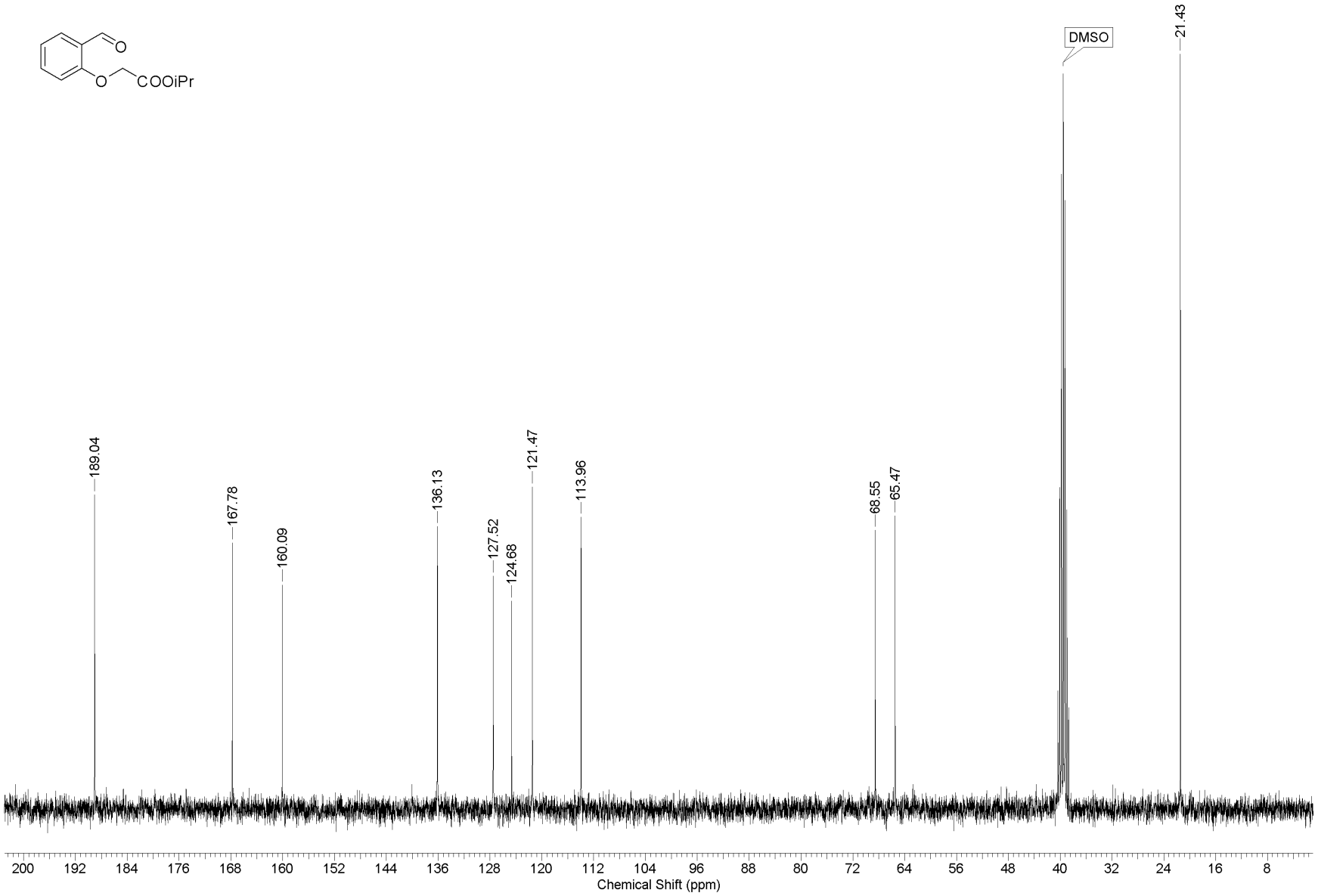
0.99
1.02
6.22
Chemical Shift (ppm)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O
COOiPr
DMSO
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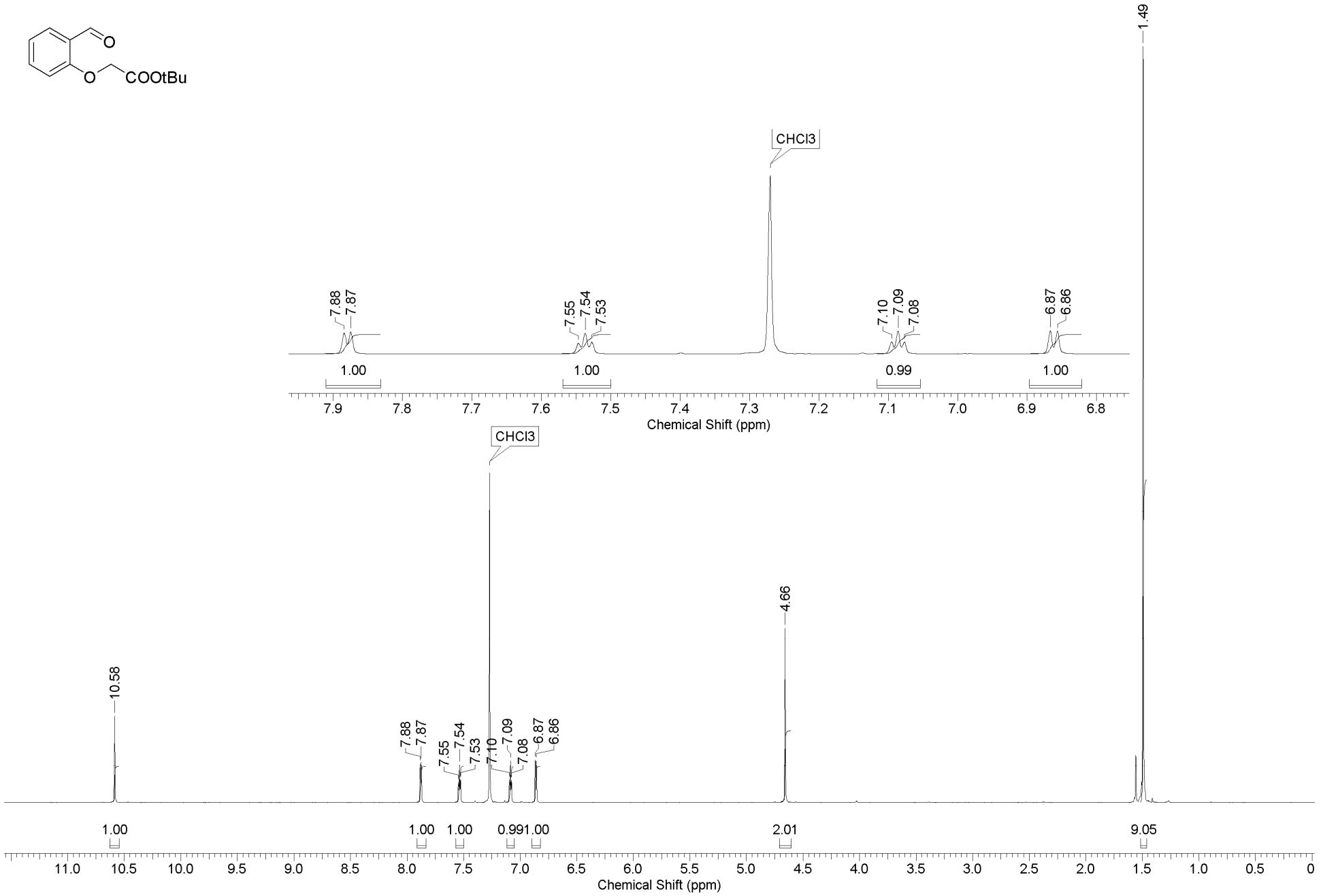
160.09
136.13
127.52
124.68
121.47
113.96
68.55
65.47
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)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O
COOtBu
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7.55
7.54
7.53
7.10
7.09
7.08
6.87
6.86
1.49
1.00
1.00
0.99
1.00
Chemical Shift (ppm)
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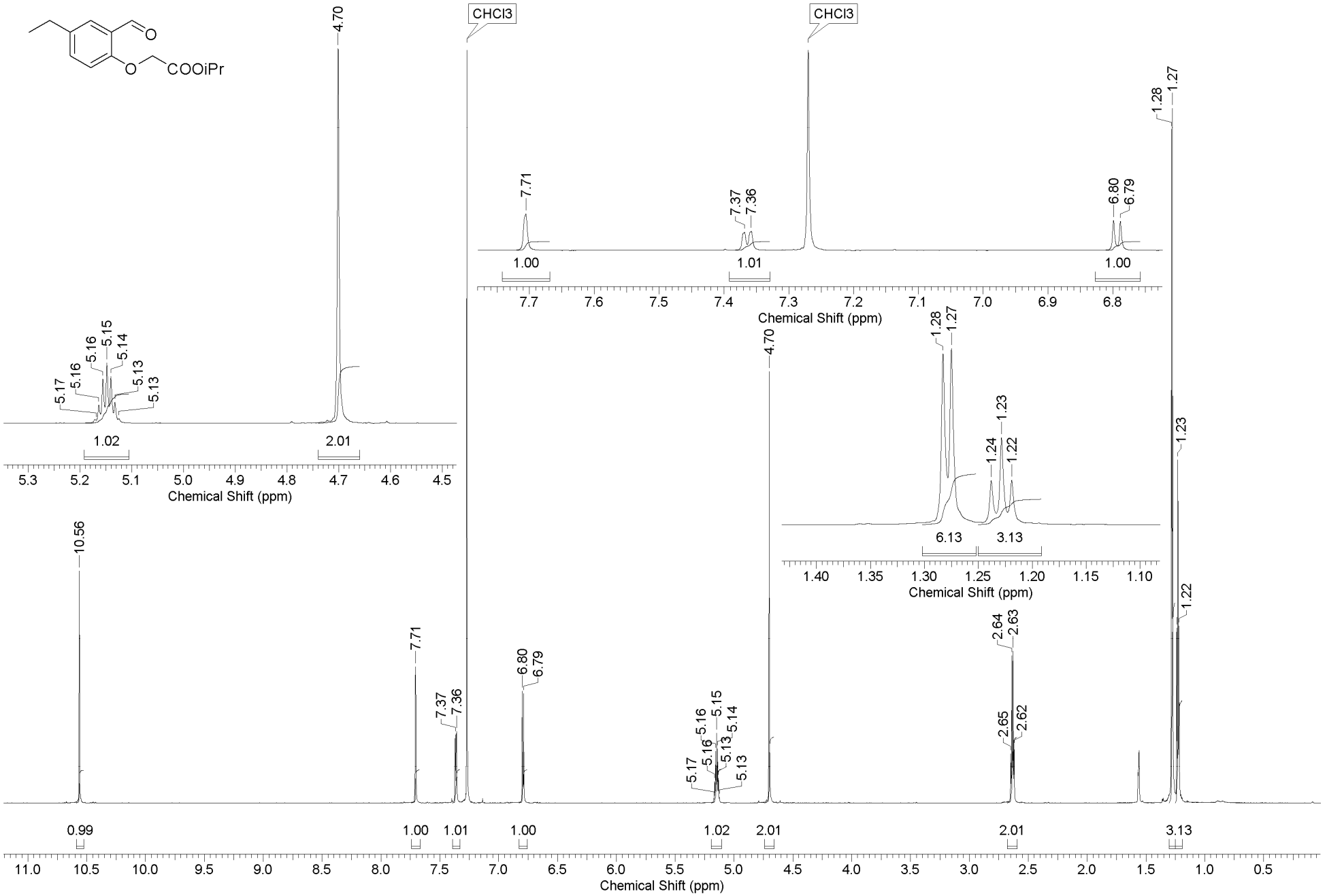
1.00
2.01
9.05
Chemical Shift (ppm)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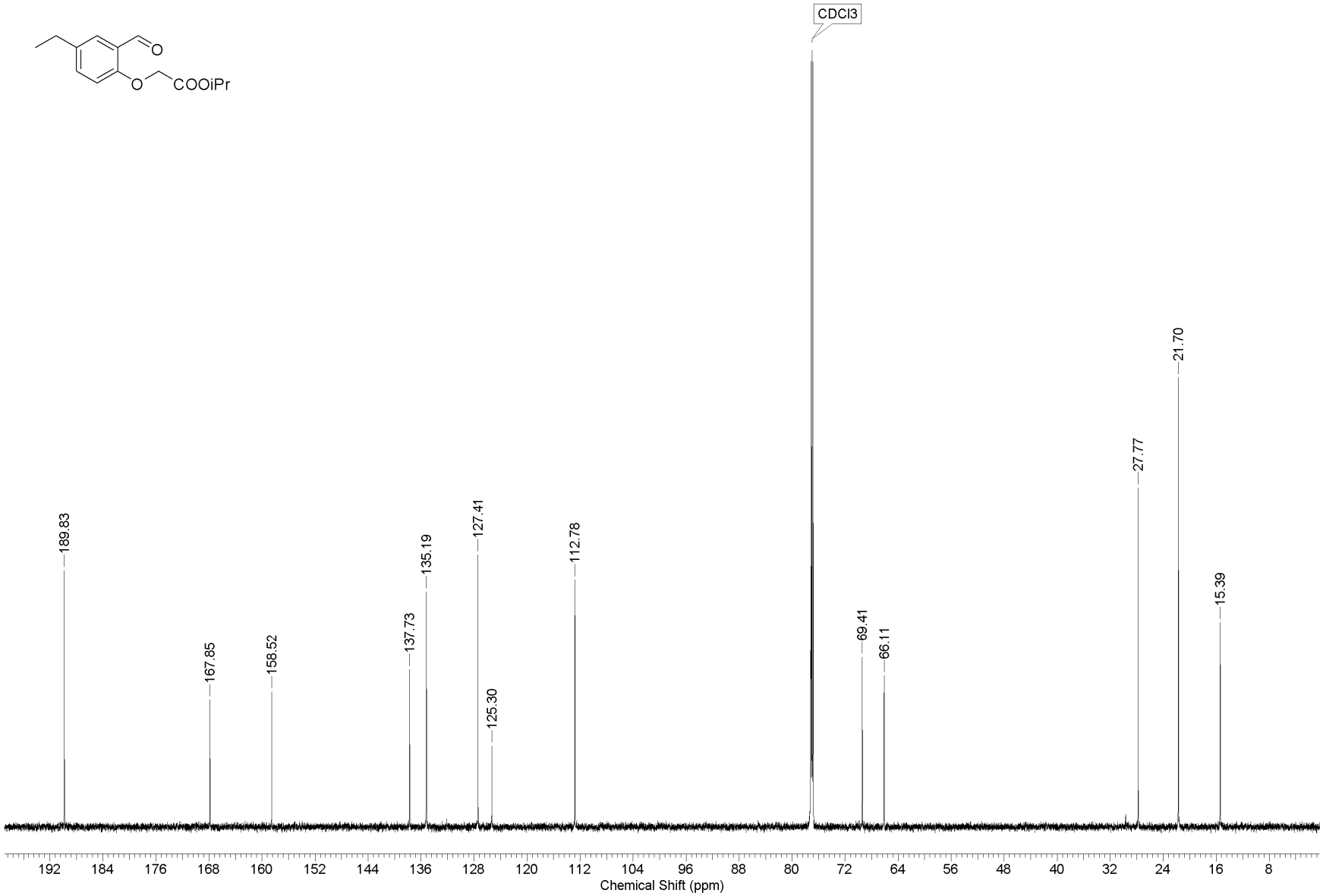
CHCl3
Chemical Shift (ppm)
Chemical Shift (ppm)
Chemical Shift (ppm)
Chemical Shift (ppm)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27.77
21.70
15.39
192
184
176
168
160
152
144
136
128
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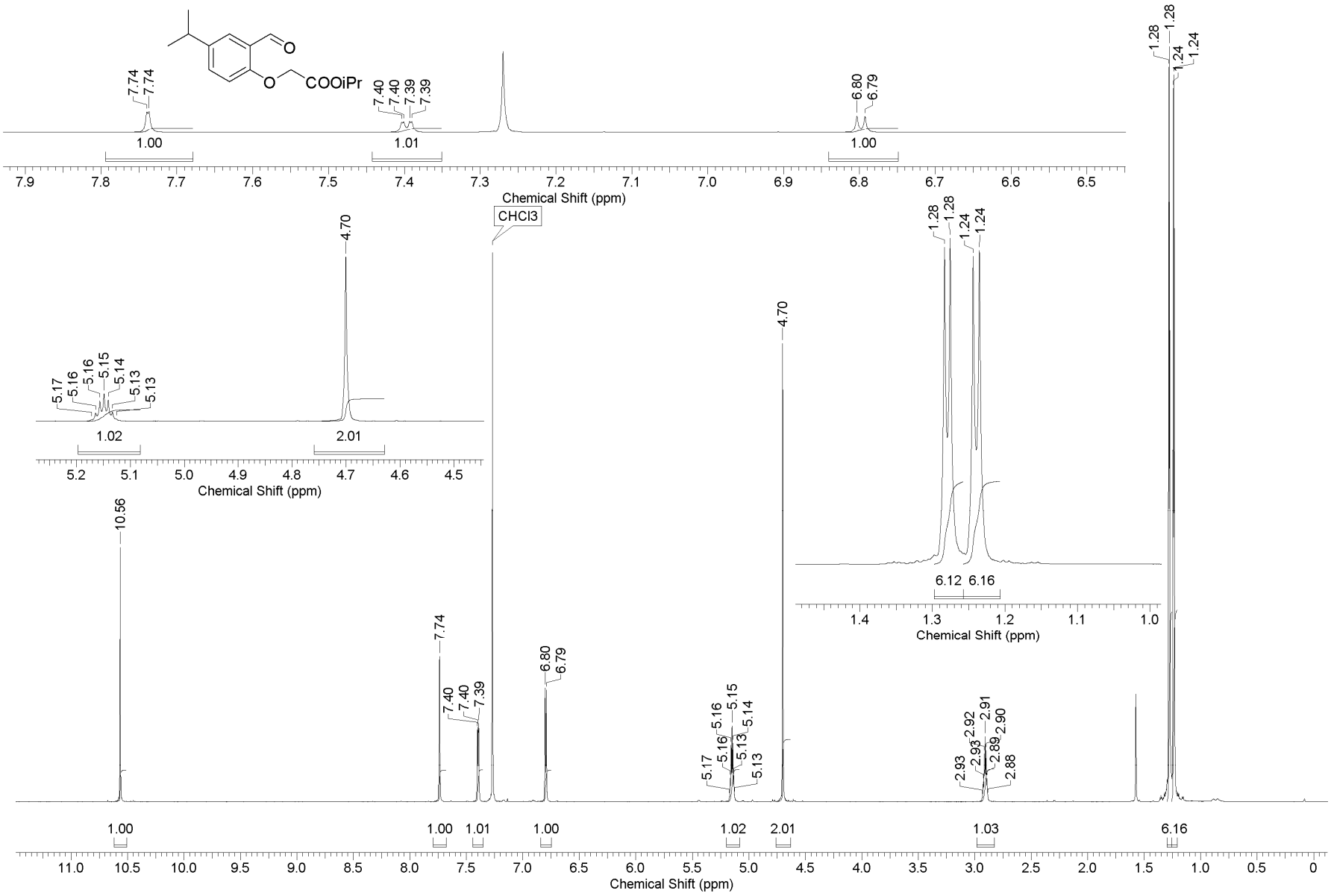
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


O
O
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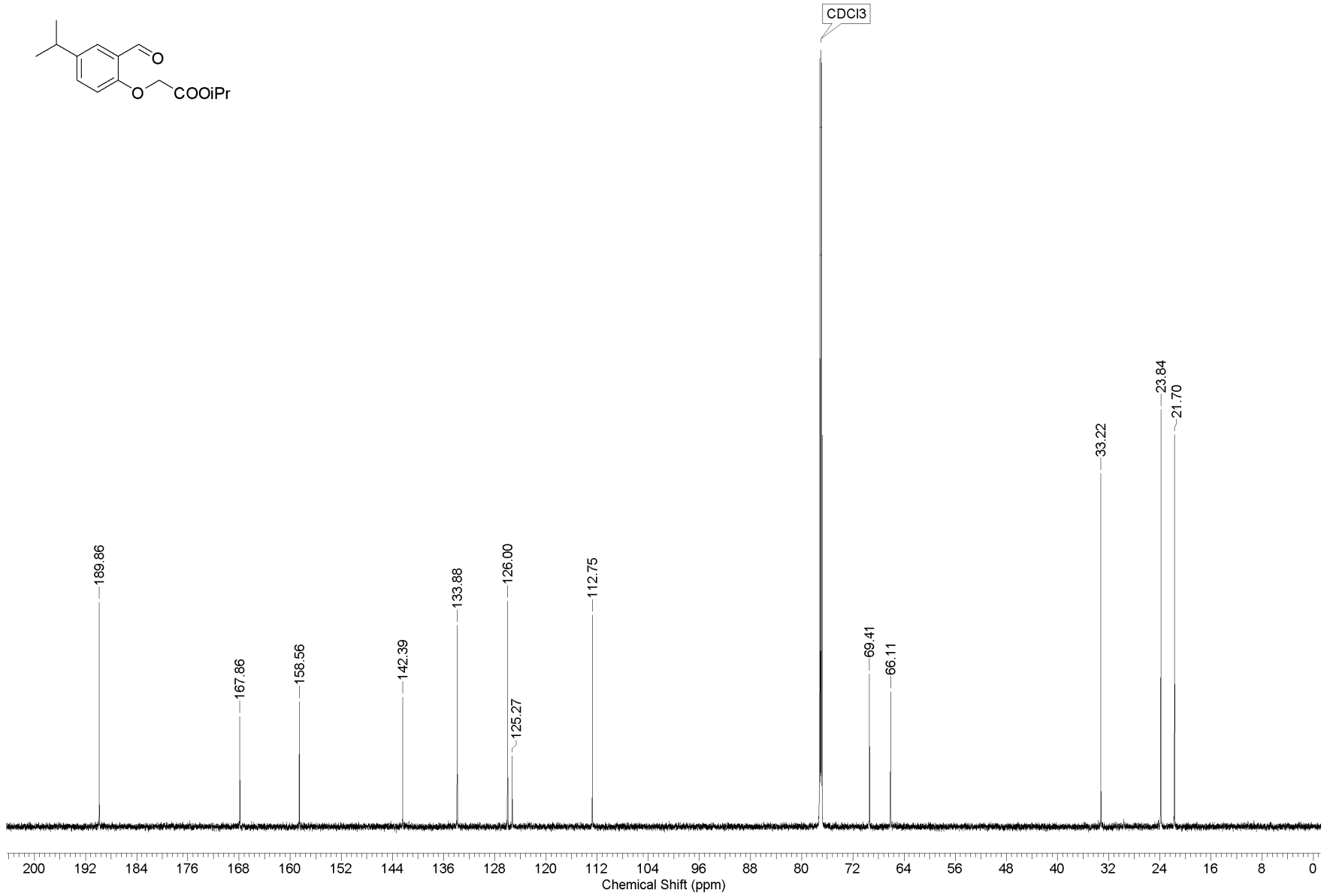
Chemical Shift (ppm)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23.84
21.70
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184
176
168
160
152
144
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96
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40
32
24
16
8
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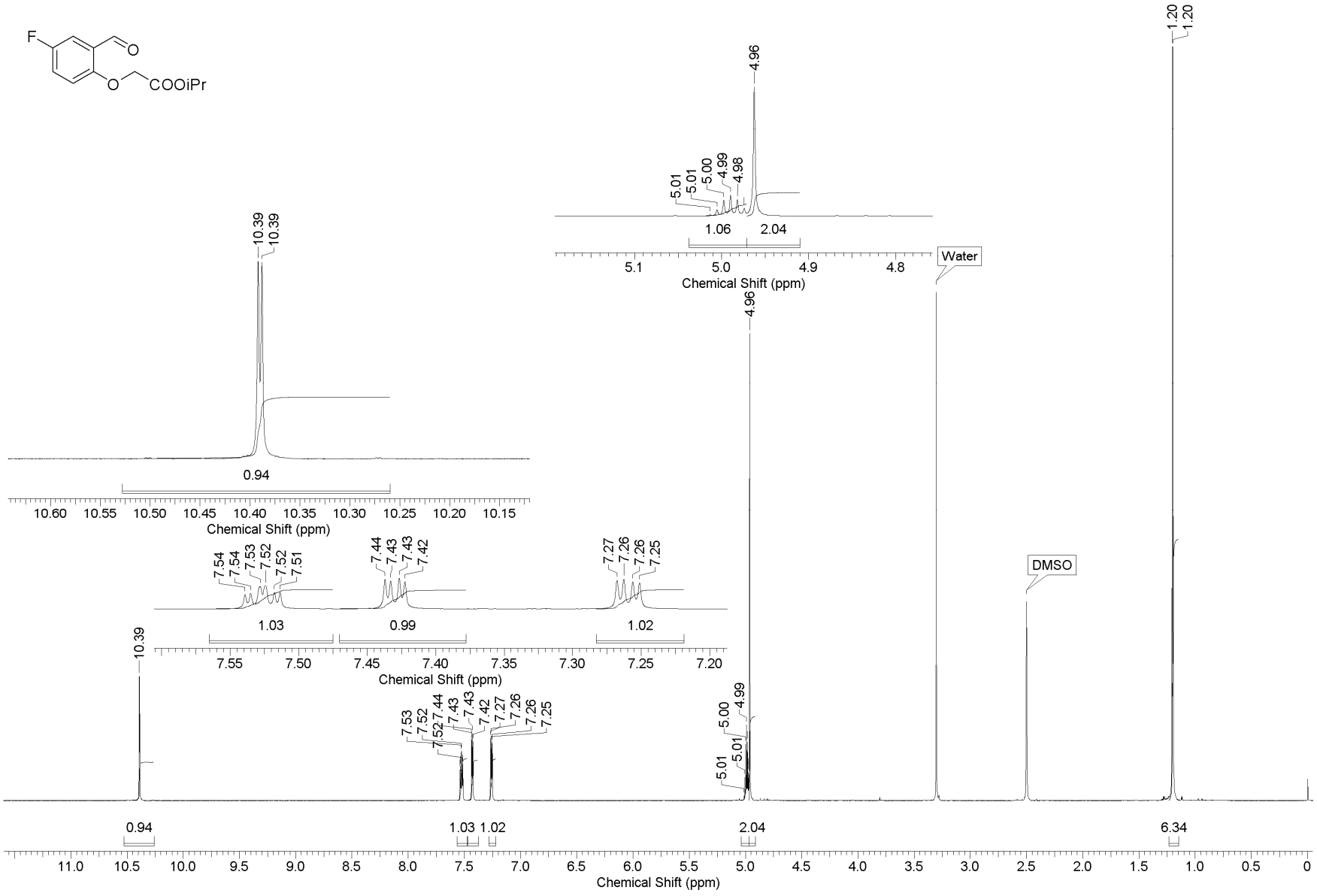
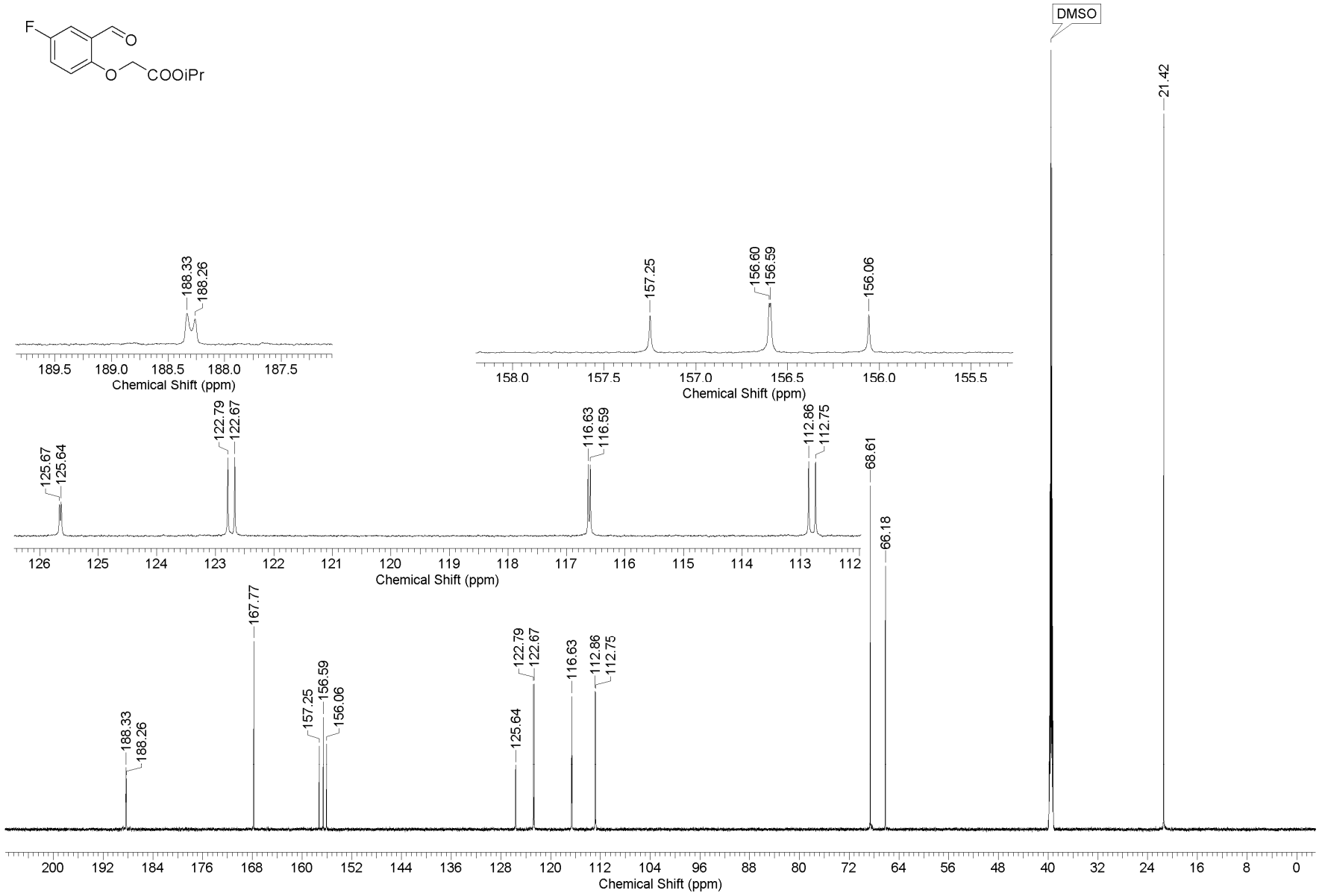
Chemical Shift (ppm)


F
O
O
COOiPr
10.39
10.39
0.94
10.60 10.55 10.50 10.45 10.40 10.35 10.30 10.25 10.20 10.15
Chemical Shift (ppm)
4.96
5.01
5.01
5.00
4.99
4.98
1.06
2.04
5.1 5.0 4.9 4.8
Chemical Shift (ppm)
Water
7.54
7.54
7.53
7.52
7.52
7.51
7.44
7.43
7.43
7.42
7.27
7.26
7.26
7.25
1.03
0.99
1.02
7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20
Chemical Shift (ppm)
DMSO
1.20
1.20
10.39
7.53
7.52
7.52
7.44
7.43
7.43
7.42
7.27
7.26
7.26
7.25
4.96
5.00
4.99
5.01
5.01
0.94
1.03
1.02
2.04
6.34
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)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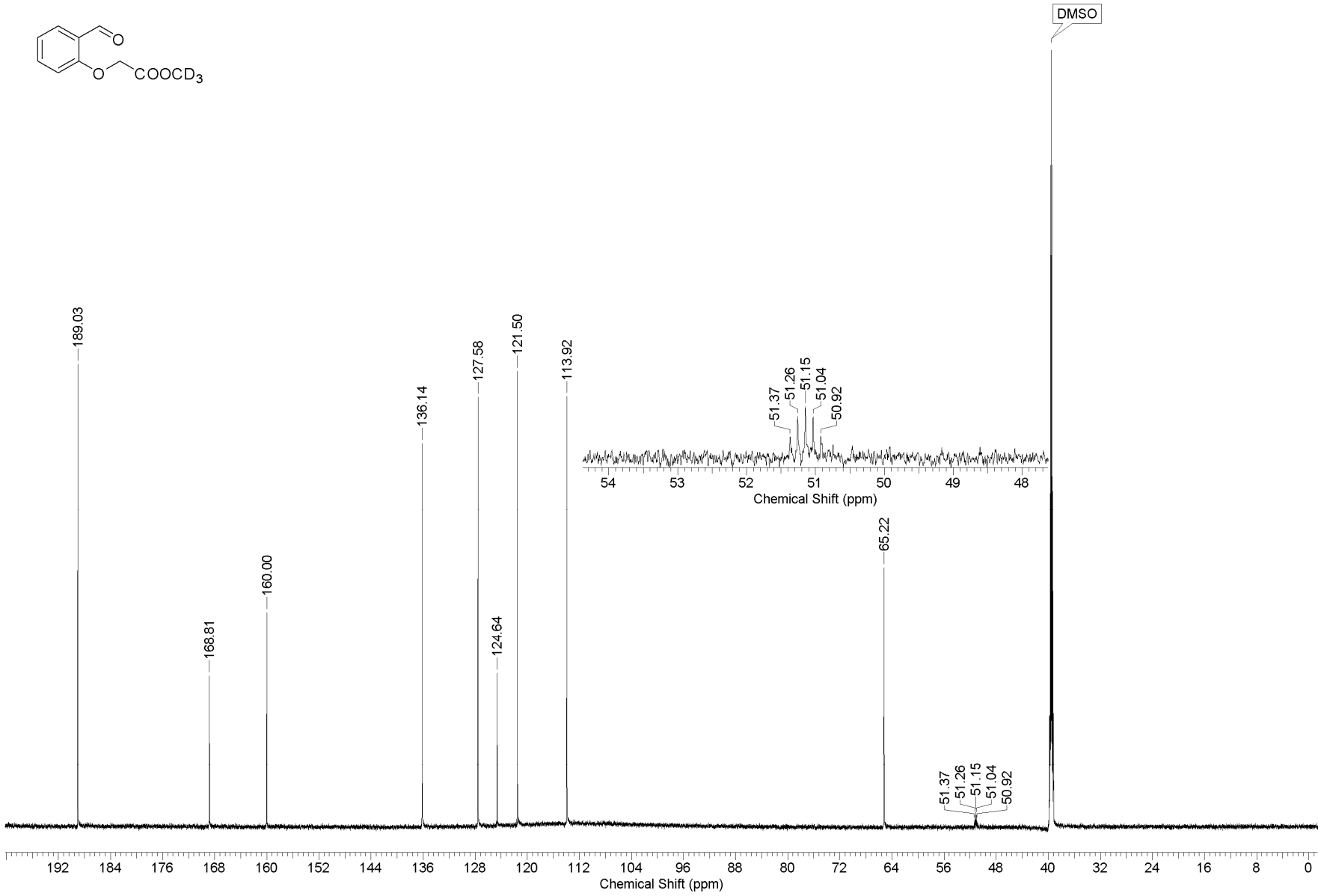
Chemical Shift (ppm)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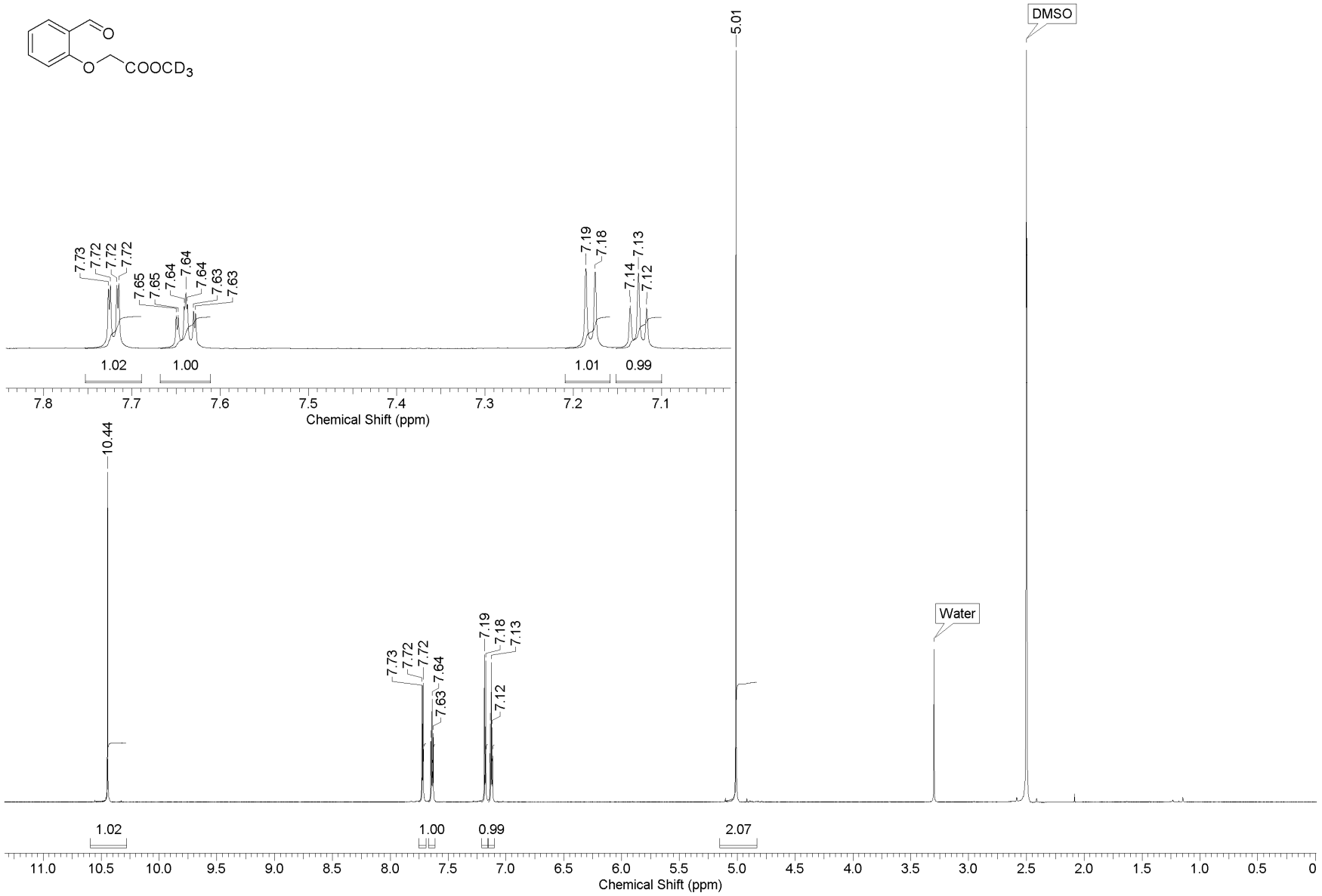
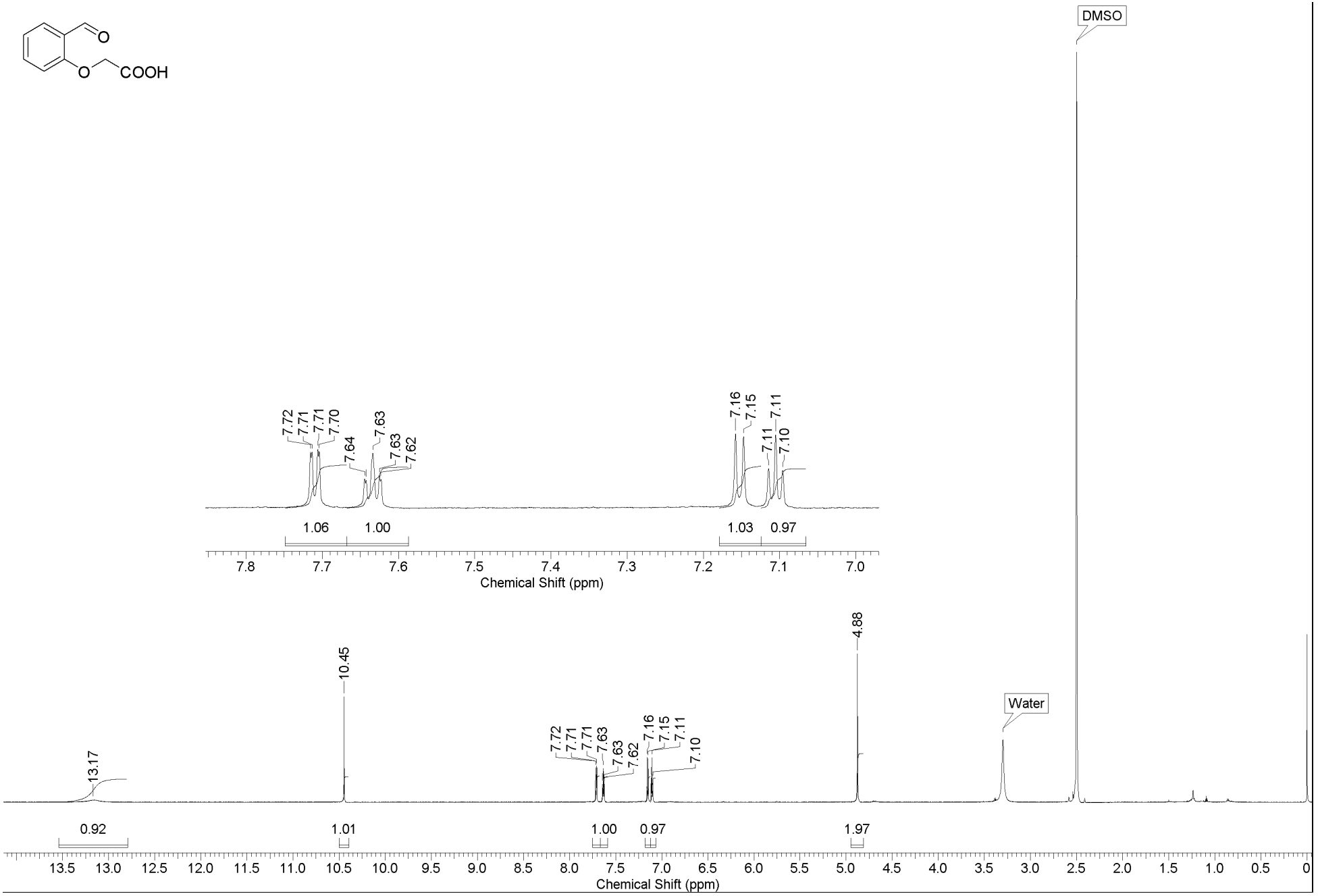
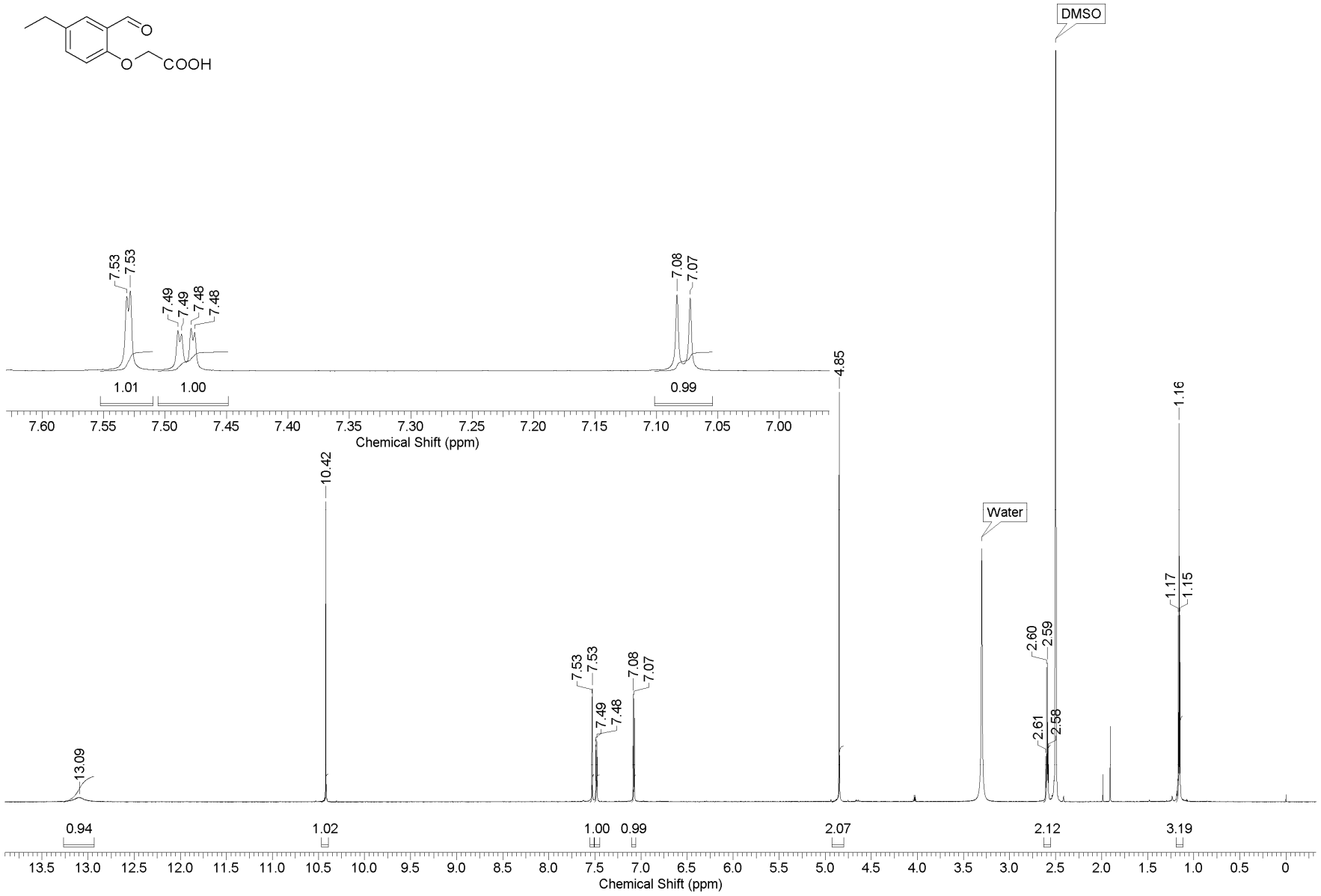
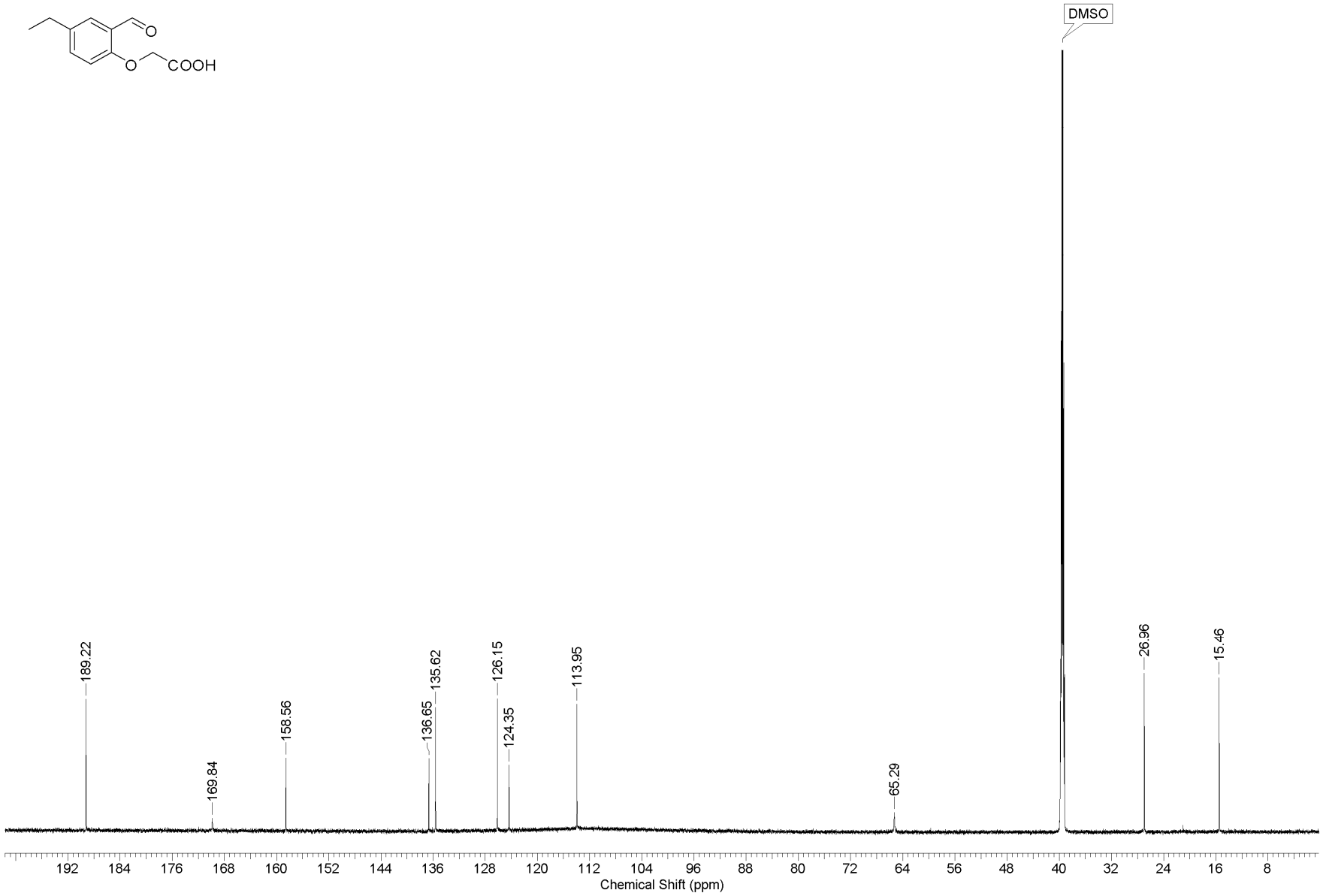
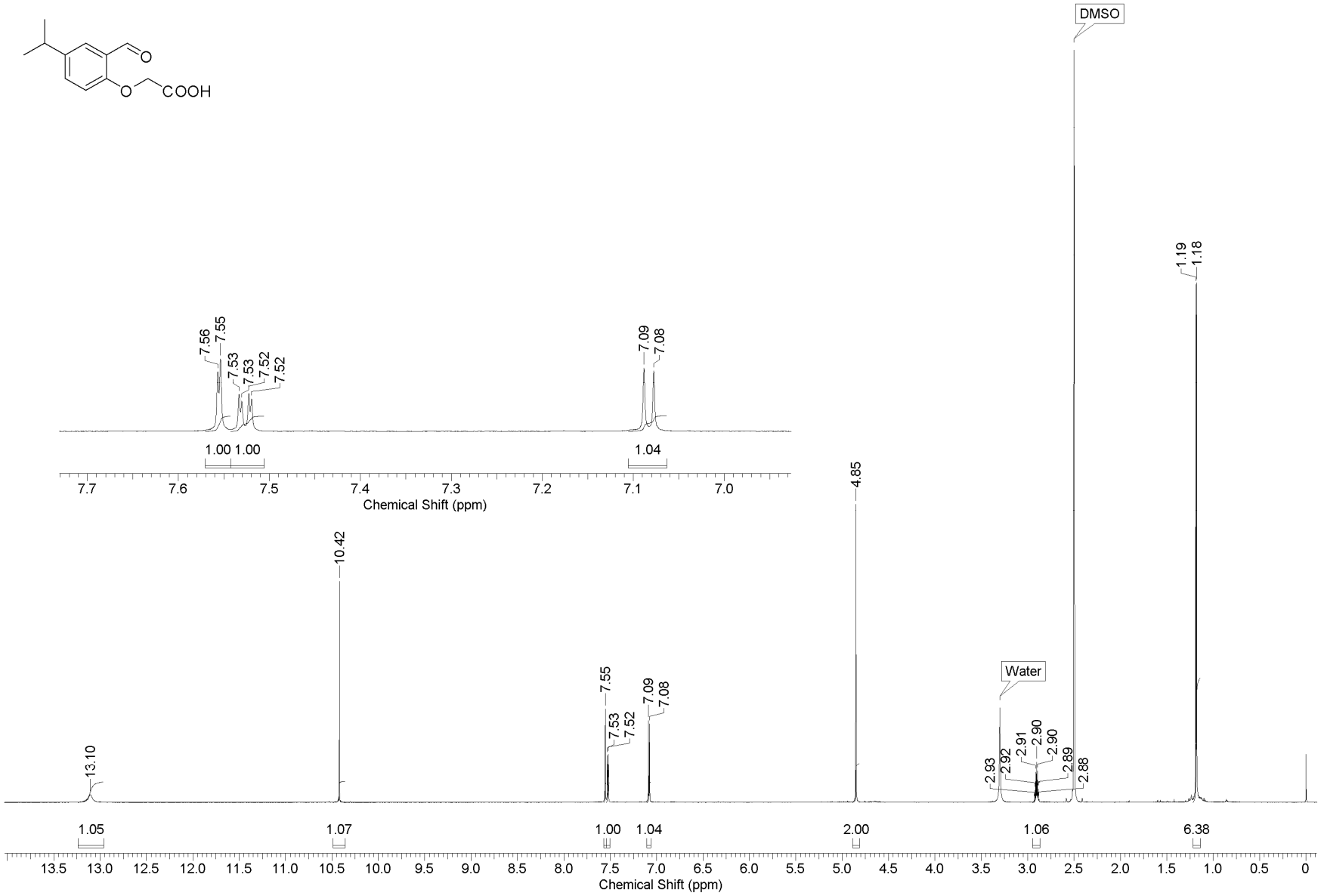
O
COOCD3
DMSO
189.03
168.81
160.00
136.14
127.58
124.64
121.50
113.92
65.22
51.37
51.26
51.15
51.04
50.92
Chemical Shift (ppm)
Chemical Shift (ppm)

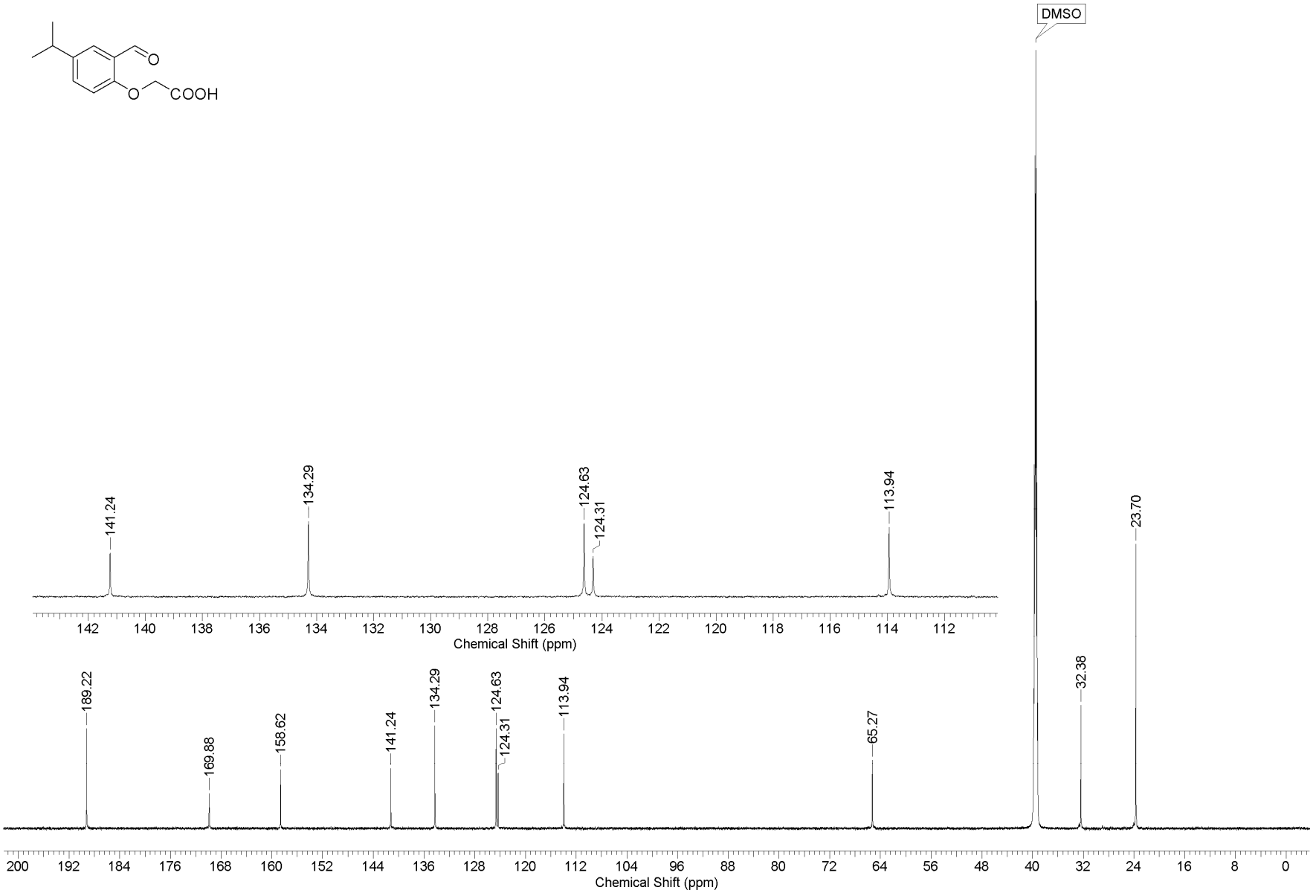

O
O
COOCD3
5.01
DMSO
Water
10.44
7.73
7.72
7.72
7.72
7.65
7.65
7.64
7.64
7.64
7.63
7.63
7.19
7.18
7.14
7.13
7.12
1.02
1.00
1.01
0.99
2.07
Chemical Shift (ppm)

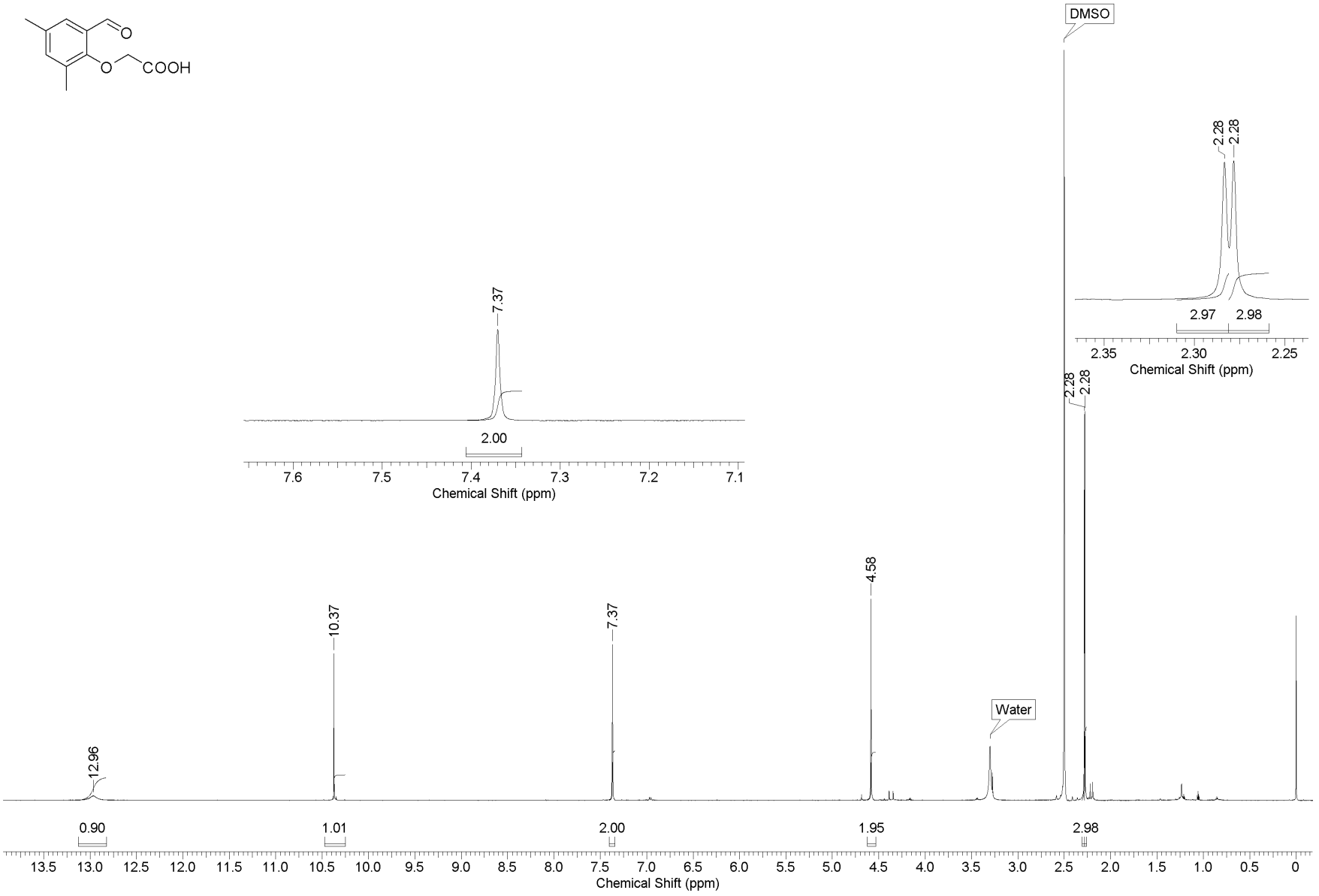

O
O
COOH
DMSO
7.72
7.71
7.71
7.70
7.64
7.63
7.63
7.62
7.16
7.15
7.11
7.11
7.10
1.06
1.00
1.03
0.97
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
Chemical Shift (ppm)
13.17
10.45
4.88
Water
0.92
1.01
1.00
0.97
1.97
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

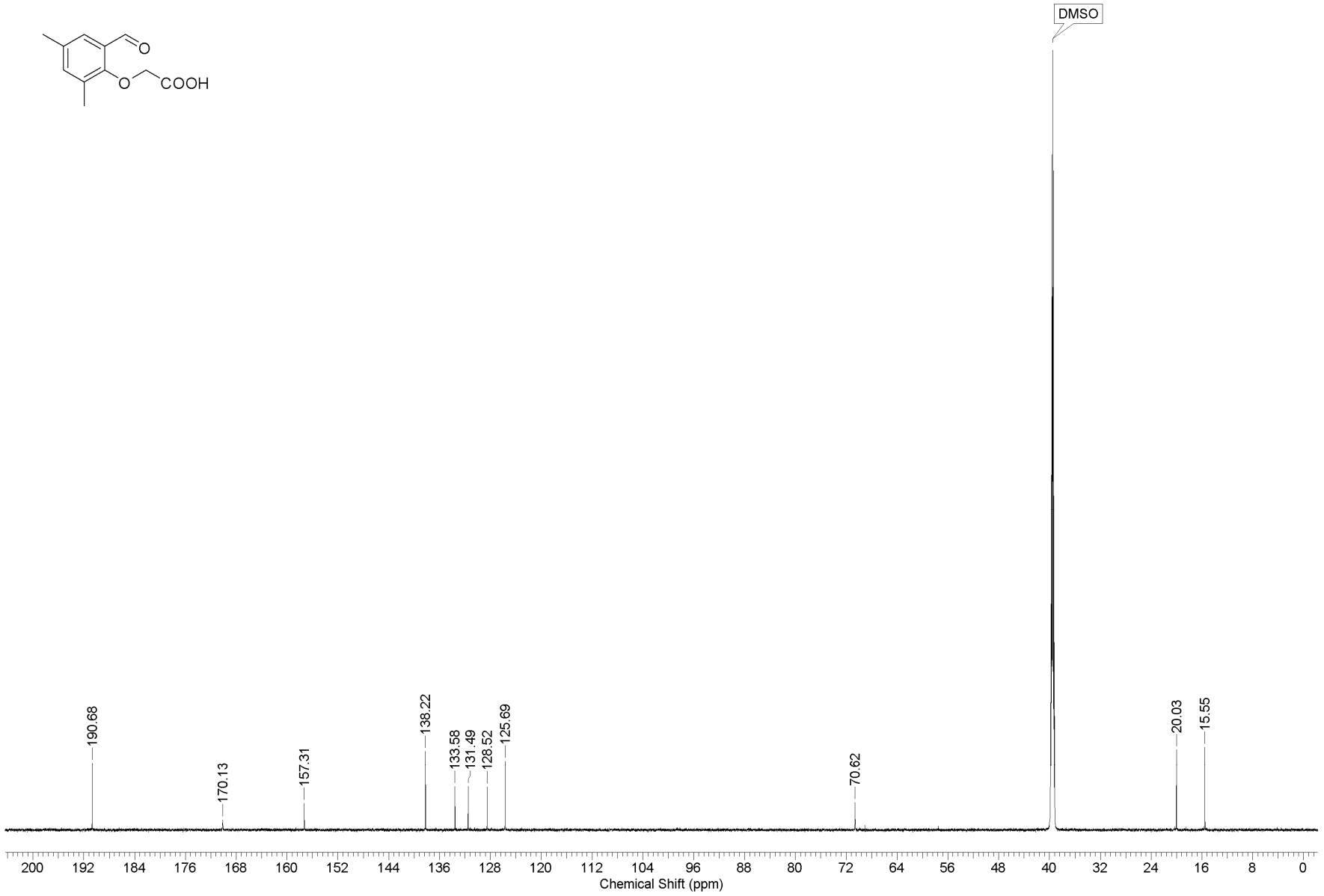

O
O
COOH
DMSO
Water
7.53
7.53
7.49
7.49
7.48
7.48
7.08
7.07
4.85
1.16
10.42
1.17
1.15
2.60
2.59
2.61
2.58
13.09
1.01
1.00
0.99
0.94
1.02
1.00
0.99
2.07
2.12
3.19
Chemical Shift (ppm)
Chemical Shift (ppm)

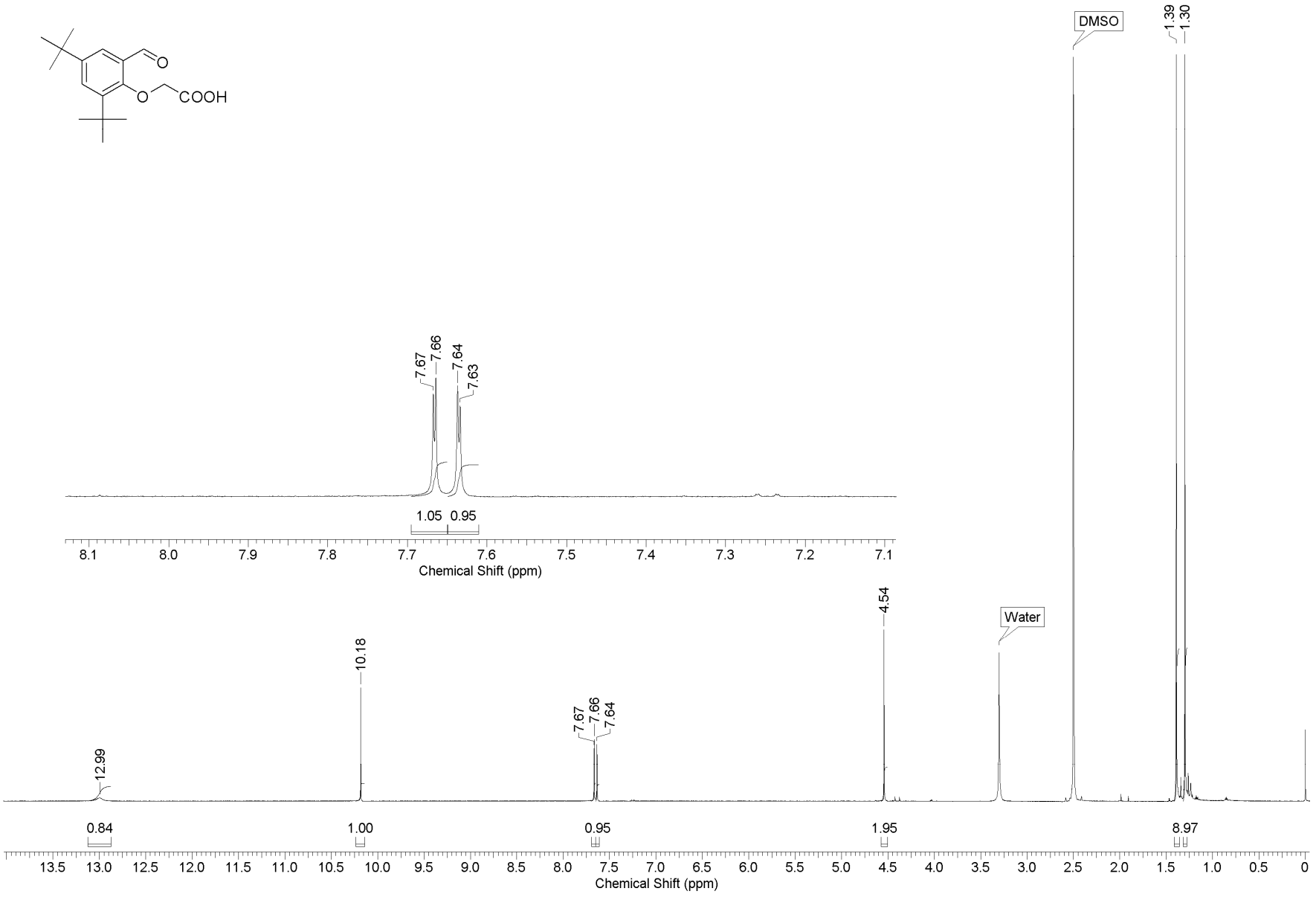

O
O
COOH
DMSO
189.22
169.84
158.56
136.65
135.62
126.15
124.35
113.95
65.29
26.96
15.46
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

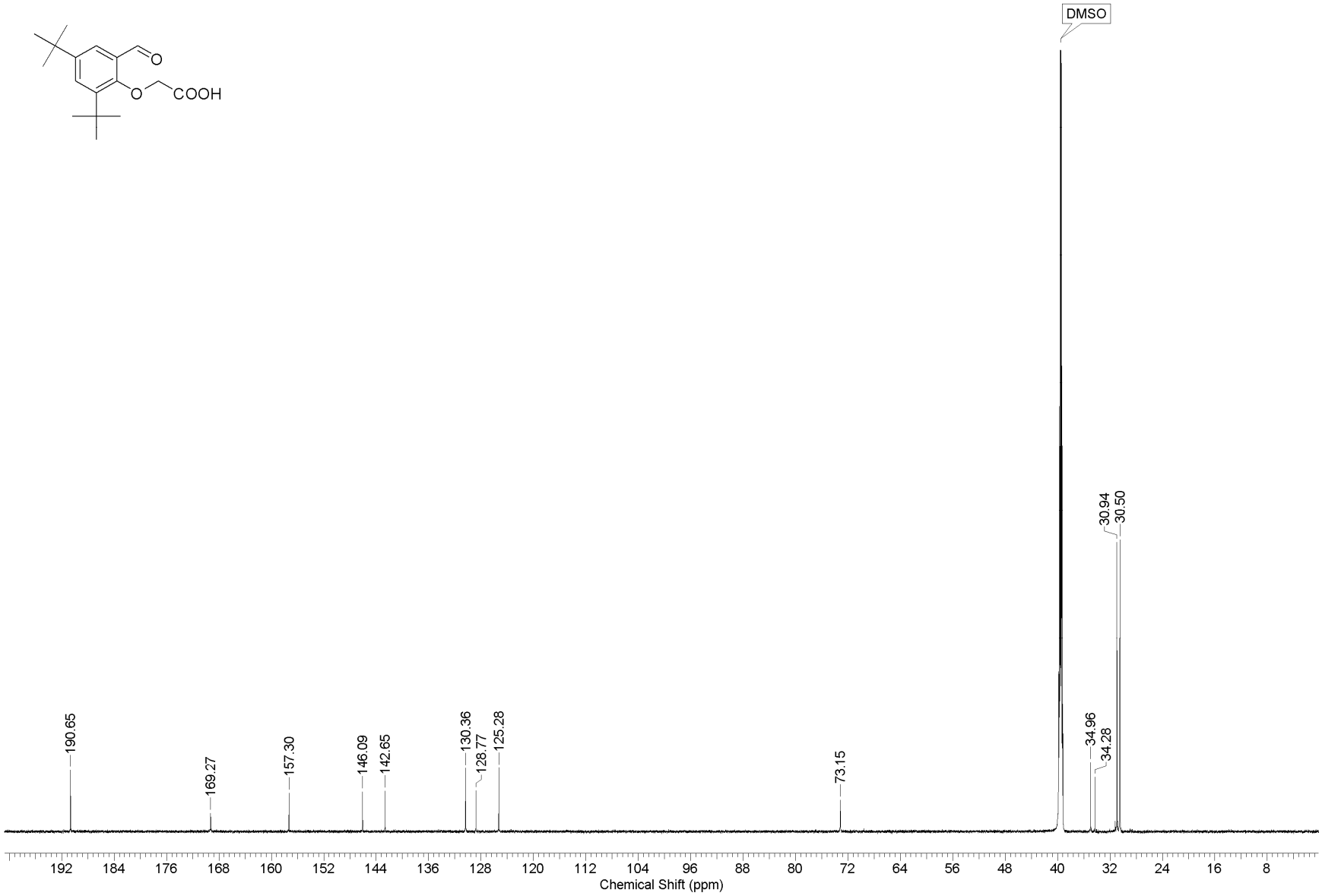

O
O
COOH
DMSO
Water
7.56
7.55
7.53
7.53
7.52
7.52
7.09
7.08
1.00 1.00
1.04
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
Chemical Shift (ppm)
13.10
10.42
7.55
7.53
7.52
7.09
7.08
4.85
2.93
2.92
2.91
2.90
2.90
2.89
2.88
1.19
1.18
1.05
1.07
1.00
1.04
2.00
1.06
6.38
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

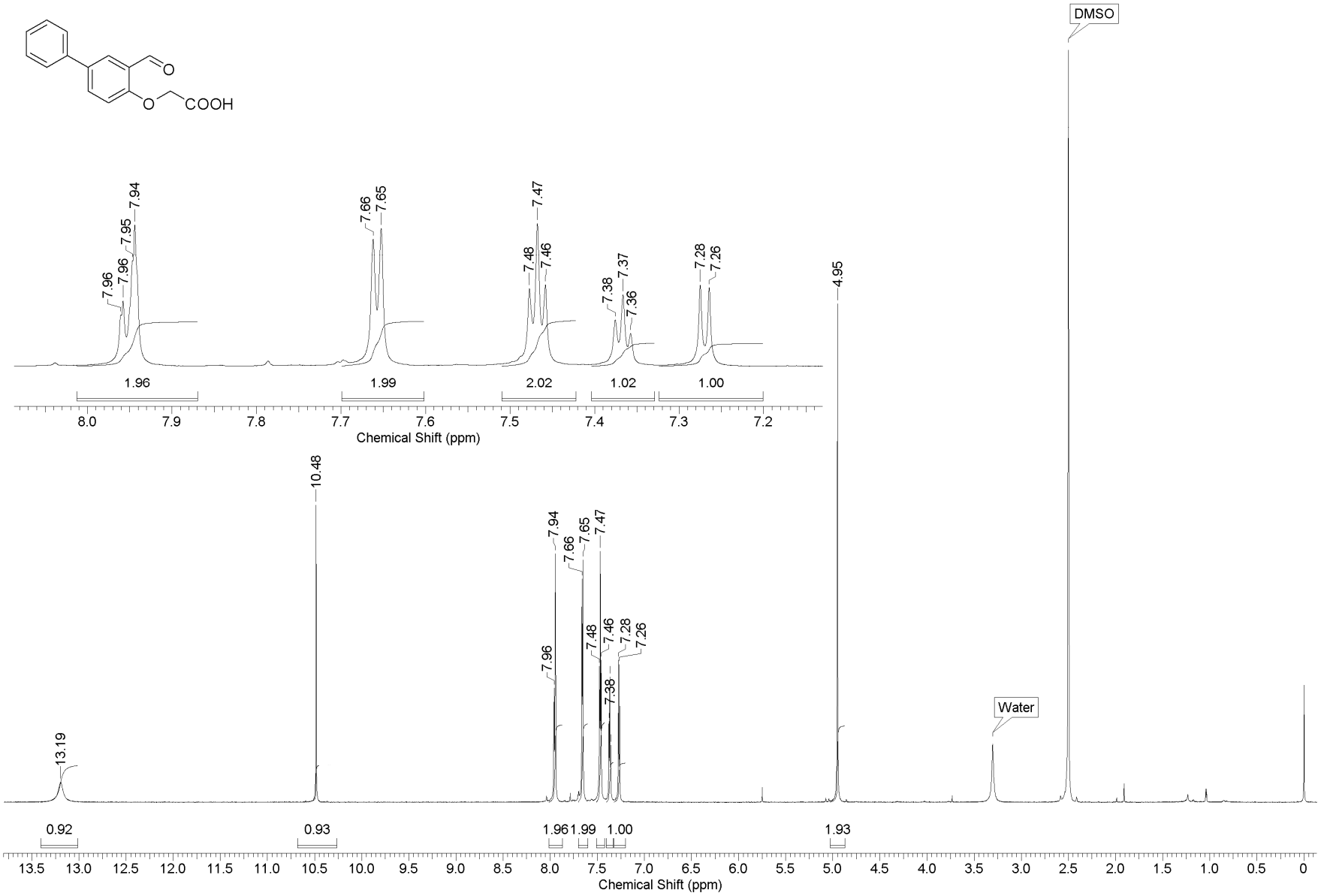

O
O
COOH
DMSO
141.24
134.29
124.63
124.31
113.94
23.70
32.38
65.27
158.62
169.88
189.22
Chemical Shift (ppm)
Chemical Shift (ppm)

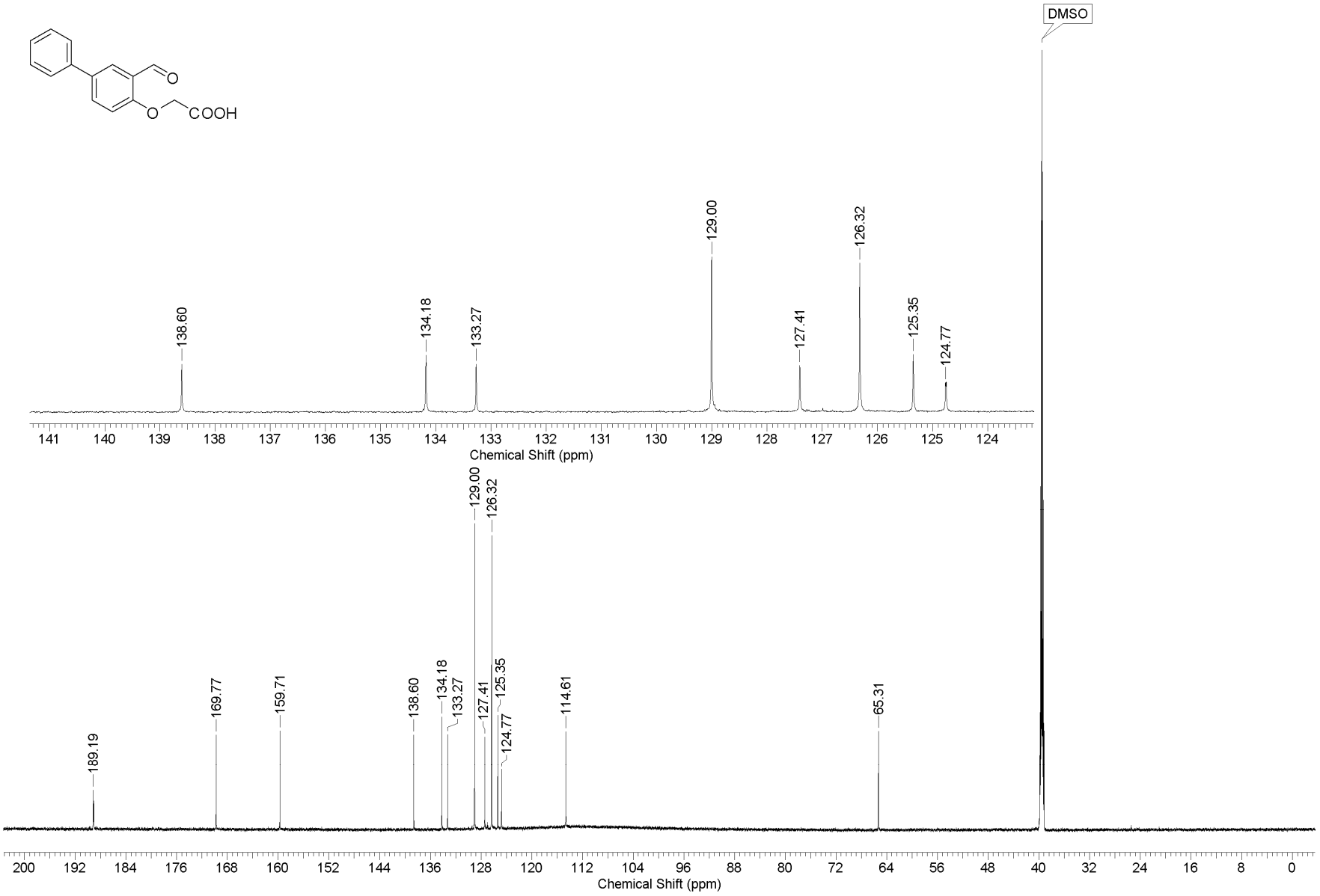

O
O
COOH
DMSO
2.28
2.28
2.97
2.98
2.35
2.30
2.25
Chemical Shift (ppm)
7.37
2.00
7.6
7.5
7.4
7.3
7.2
7.1
Chemical Shift (ppm)
2.28
2.28
4.58
10.37
7.37
Water
12.96
0.90
1.01
2.00
1.95
2.98
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

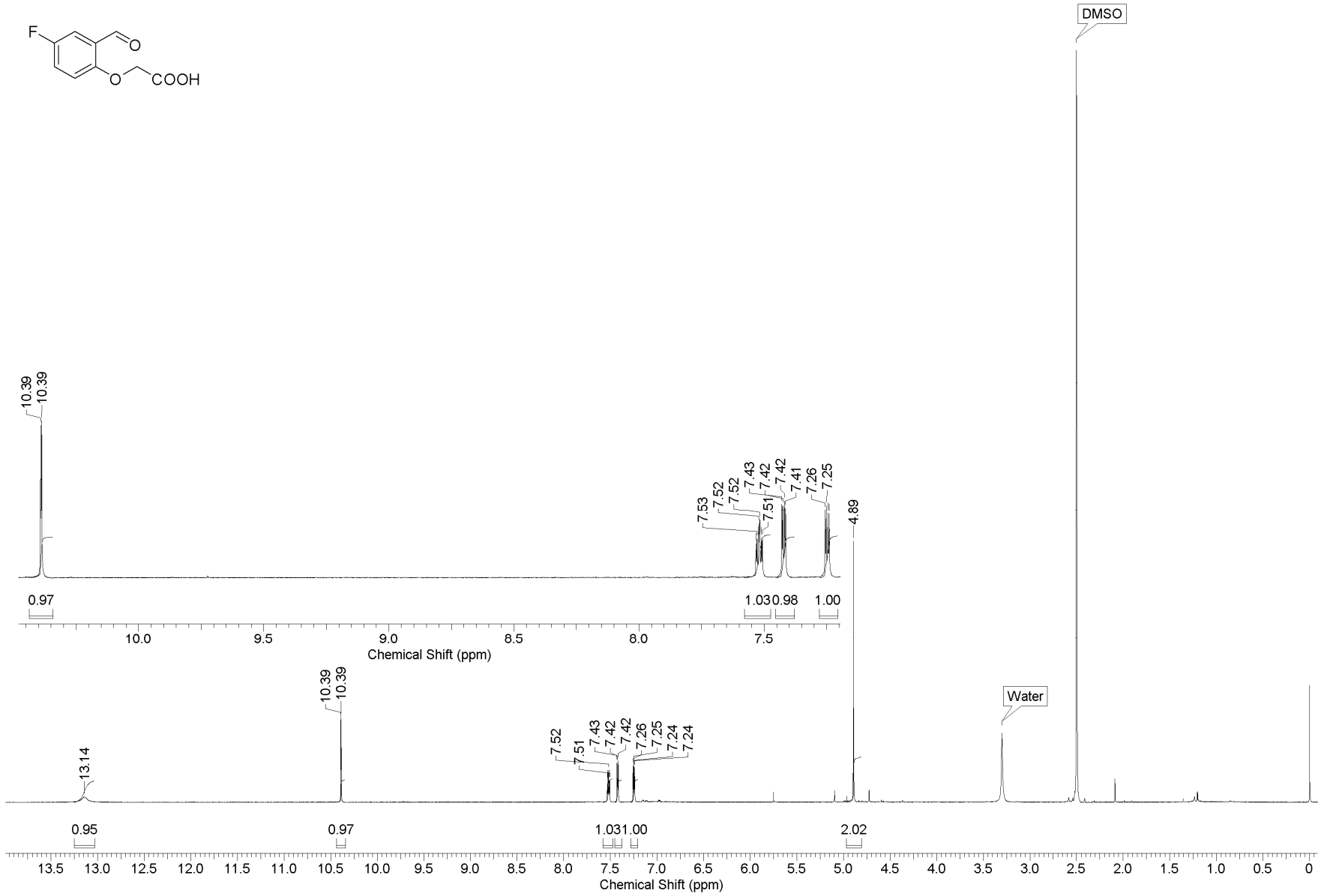

O
O
COOH
DMSO
190.68
170.13
157.31
138.22
133.58
131.49
128.52
125.69
70.62
20.03
15.55
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

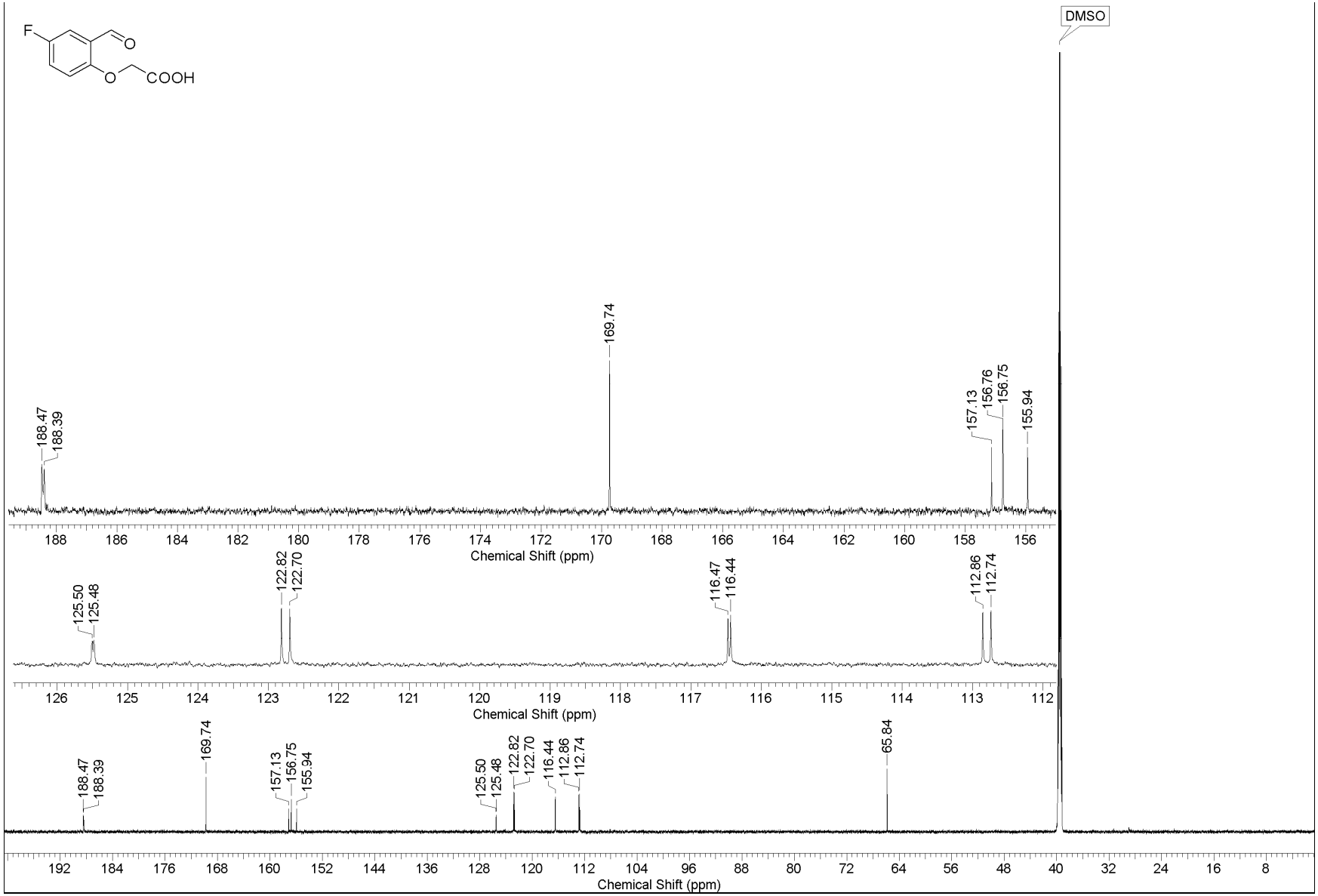

O
O
COOH
DMSO
1.39
1.30
7.67
7.66
7.64
7.63
1.05
0.95
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
Chemical Shift (ppm)
4.54
Water
10.18
7.67
7.66
7.64
12.99
0.84
1.00
0.95
1.95
8.97
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

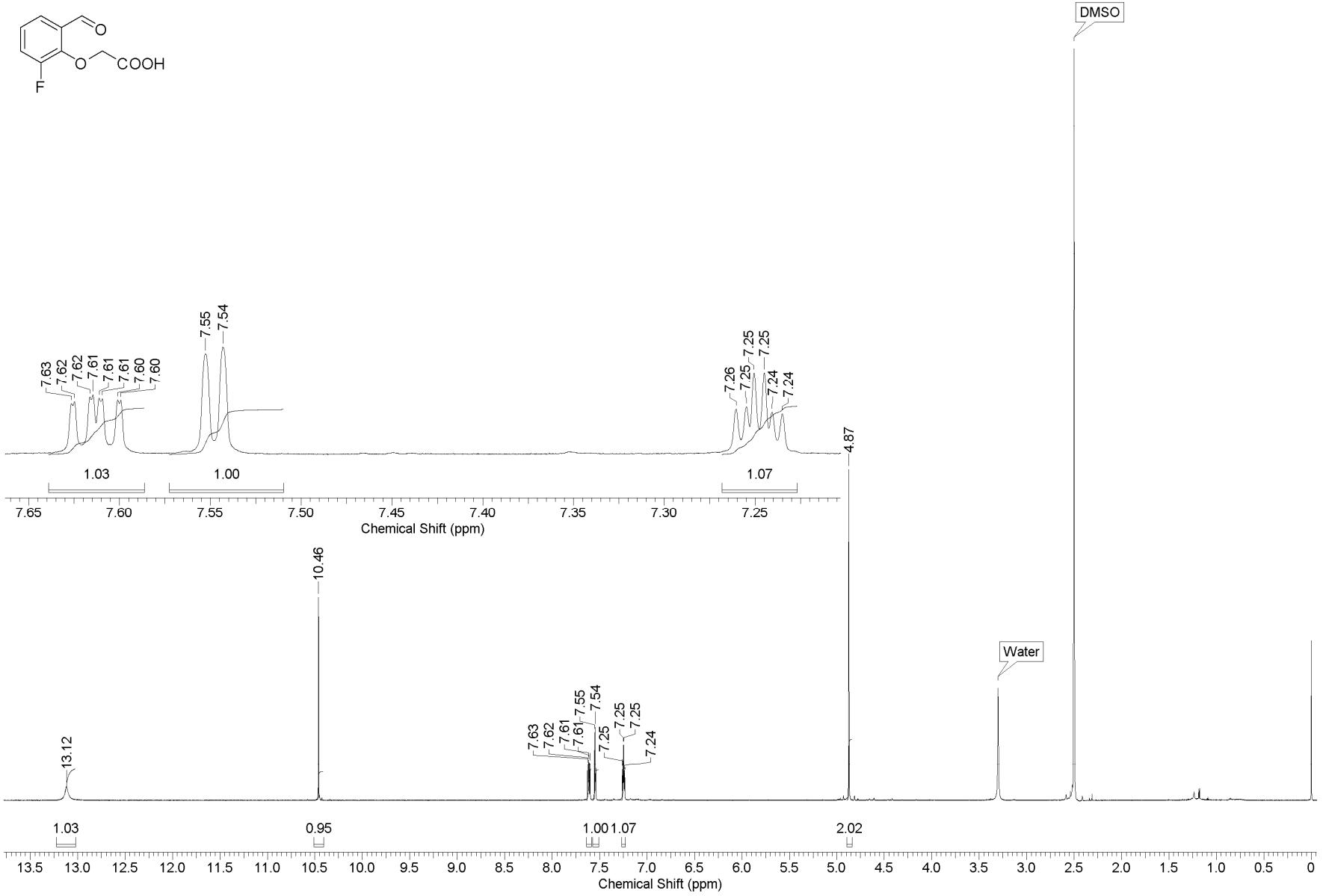

O
O
COOH
DMSO
190.65
169.27
157.30
146.09
142.65
130.36
128.77
125.28
73.15
34.96
34.28
30.94
30.50
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

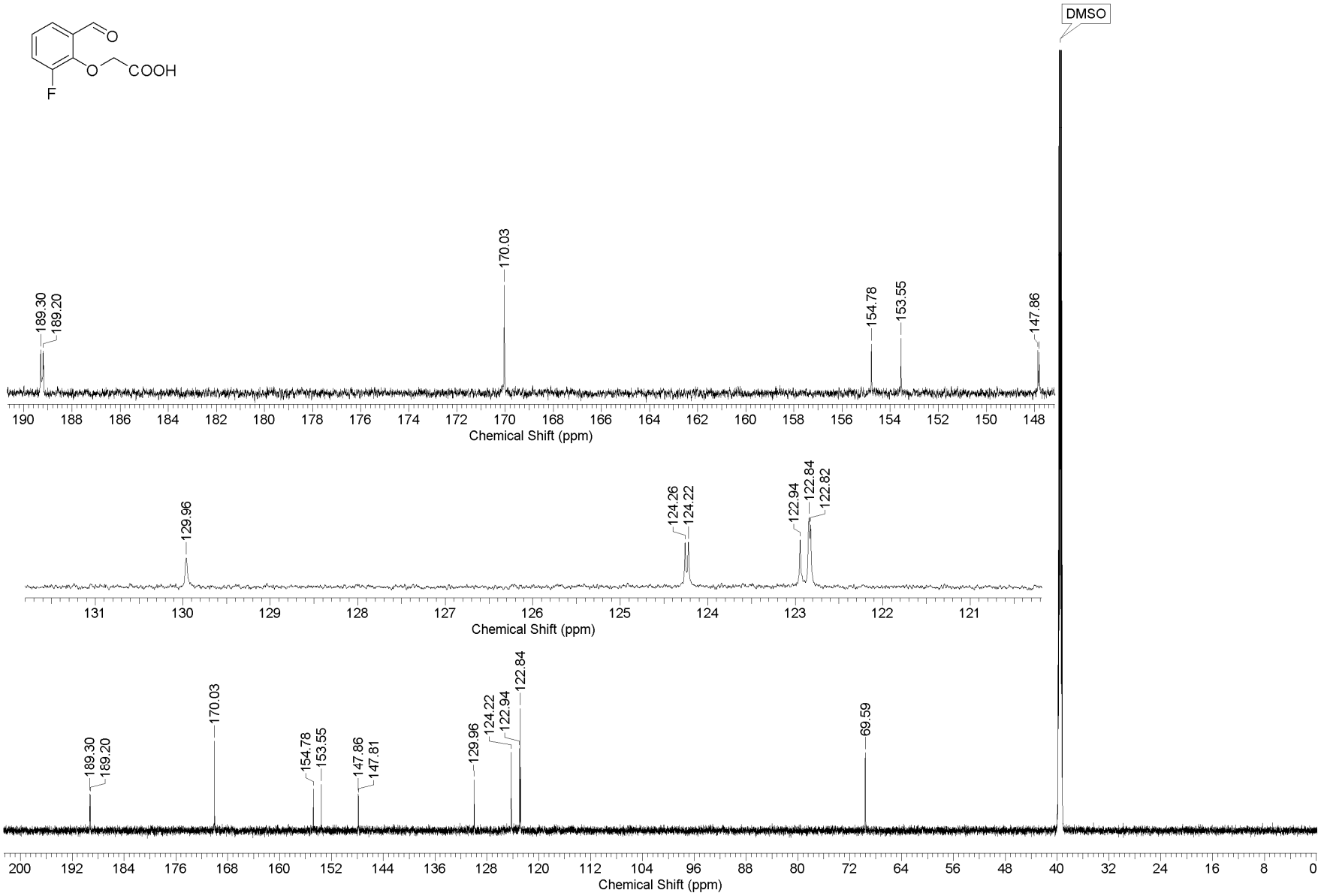

O
O
COOH
DMSO
Water
7.96
7.96
7.95
7.94
7.66
7.65
7.48
7.47
7.46
7.38
7.37
7.36
7.28
7.26
4.95
1.96
1.99
2.02
1.02
1.00
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
Chemical Shift (ppm)
10.48
13.19
0.92
0.93
1.96
1.99
1.00
1.93
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

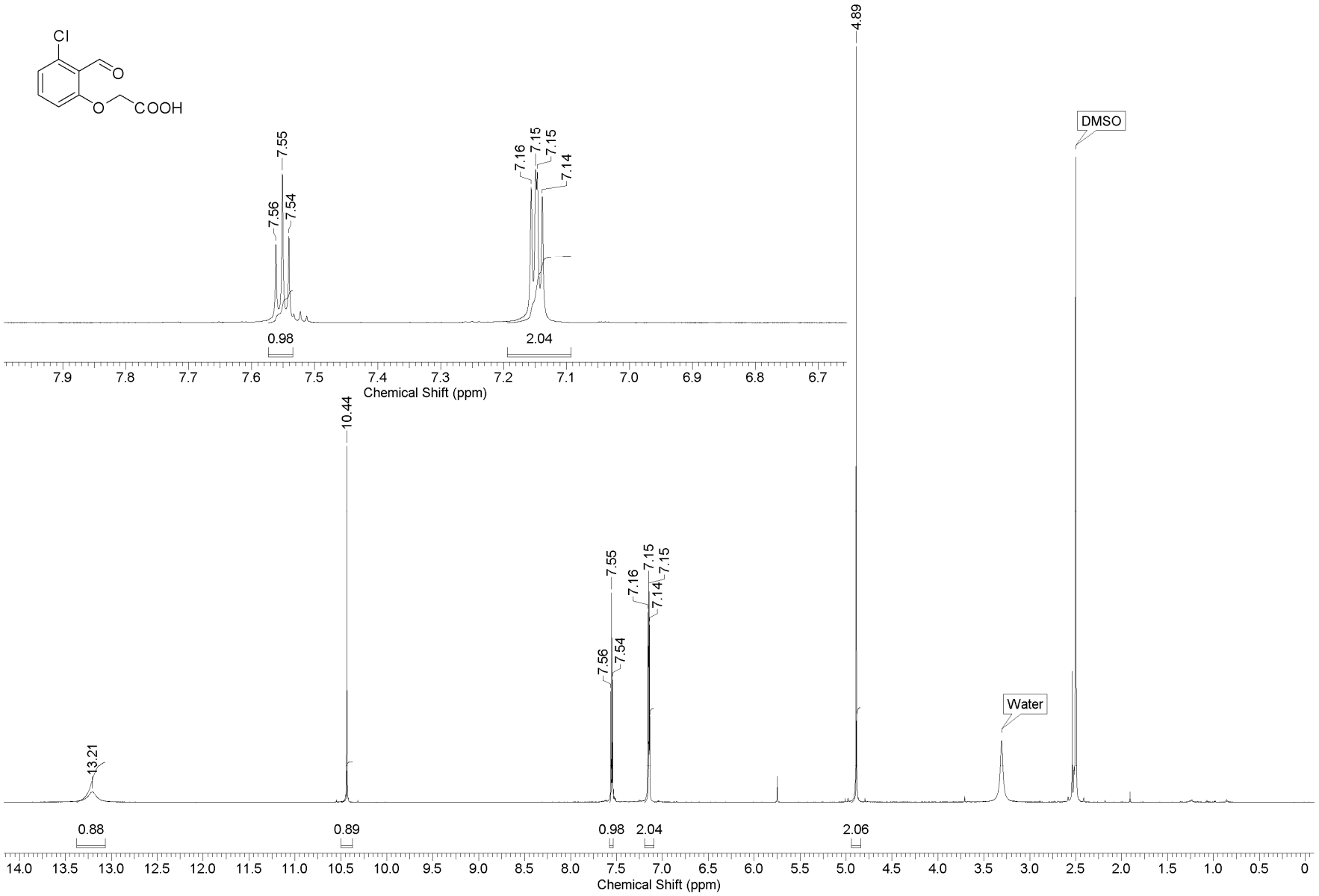

O
O
COOH
DMSO
138.60
134.18
133.27
129.00
127.41
126.32
125.35
124.77
Chemical Shift (ppm)
189.19
169.77
159.71
138.60
134.18
133.27
129.00
126.32
127.41
125.35
124.77
114.61
65.31
Chemical Shift (ppm)

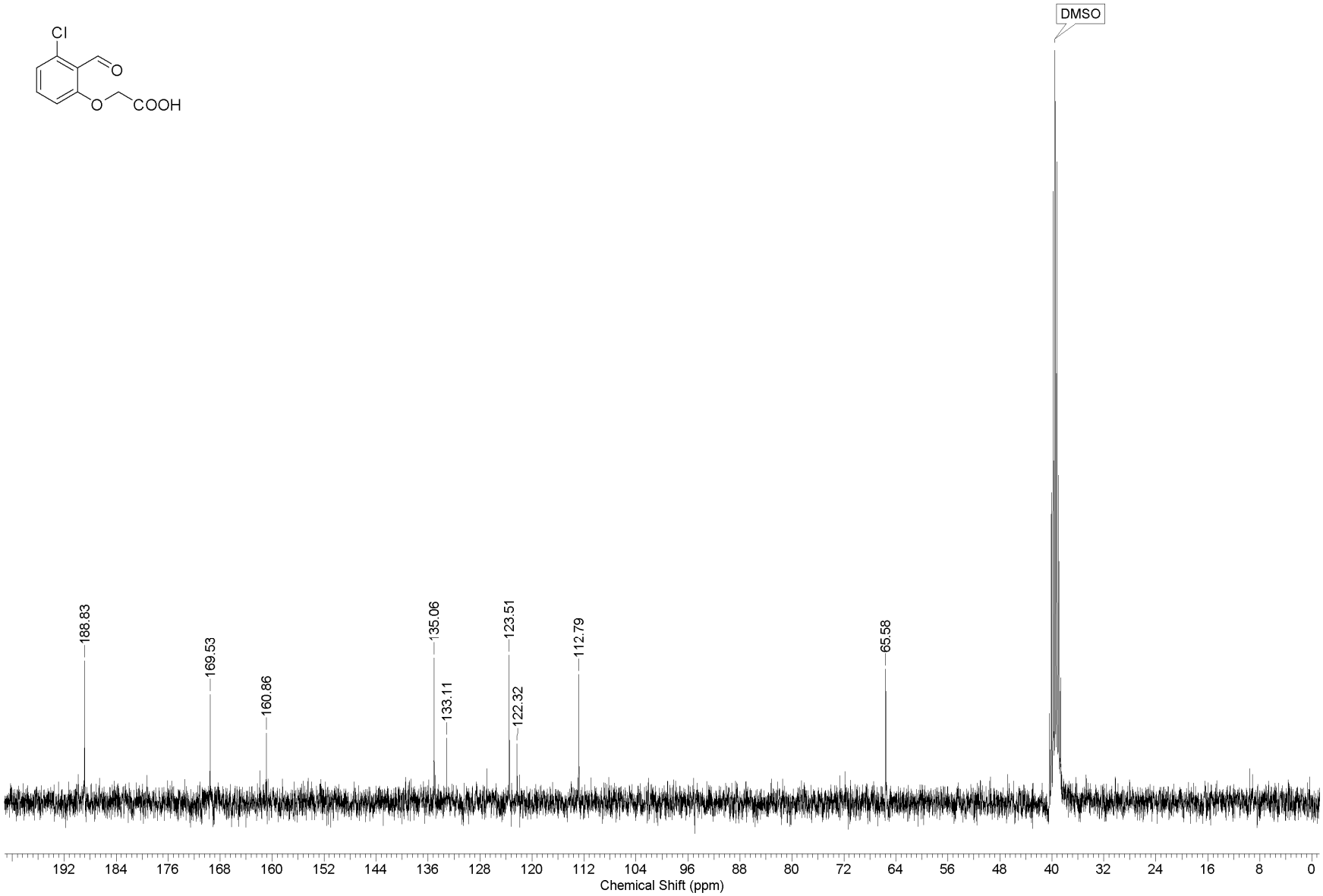

F
O
O
COOH
DMSO
10.39
10.39
7.53
7.52
7.52
7.51
7.43
7.42
7.42
7.41
7.26
7.25
4.89
0.97
1.03
0.98
1.00
10.0
9.5
9.0
8.5
8.0
7.5
Chemical Shift (ppm)
13.14
10.39
10.39
7.52
7.51
7.43
7.42
7.42
7.26
7.25
7.24
7.24
Water
0.95
0.97
1.03
1.00
2.02
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

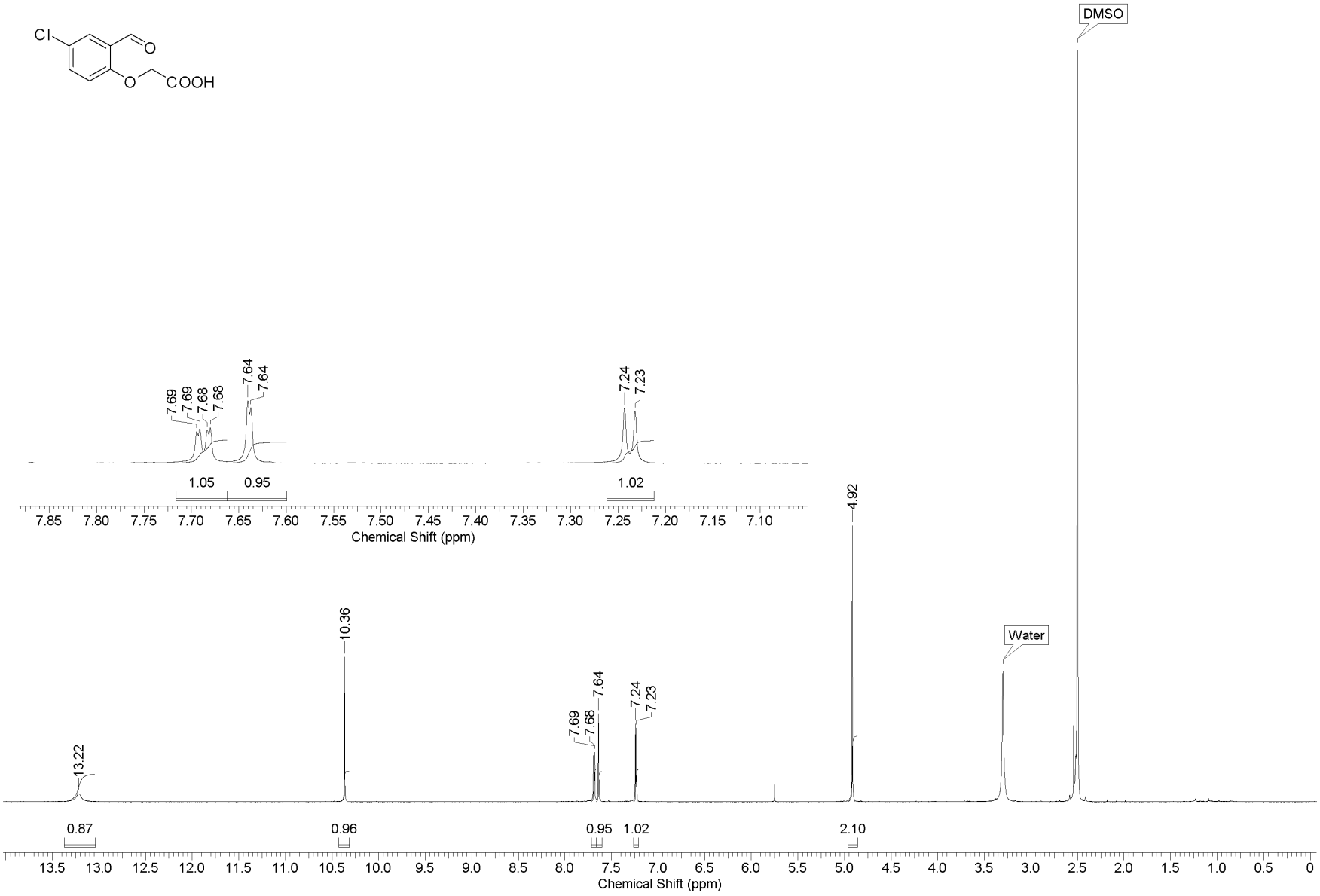

F
O
O
COOH
DMSO
188.47
188.39
169.74
157.13
156.76
156.75
155.94
Chemical Shift (ppm)
125.50
125.48
122.82
122.70
116.47
116.44
112.86
112.74
Chemical Shift (ppm)
188.47
188.39
169.74
157.13
156.75
155.94
125.50
125.48
122.82
122.70
116.44
112.86
112.74
65.84
Chemical Shift (ppm)

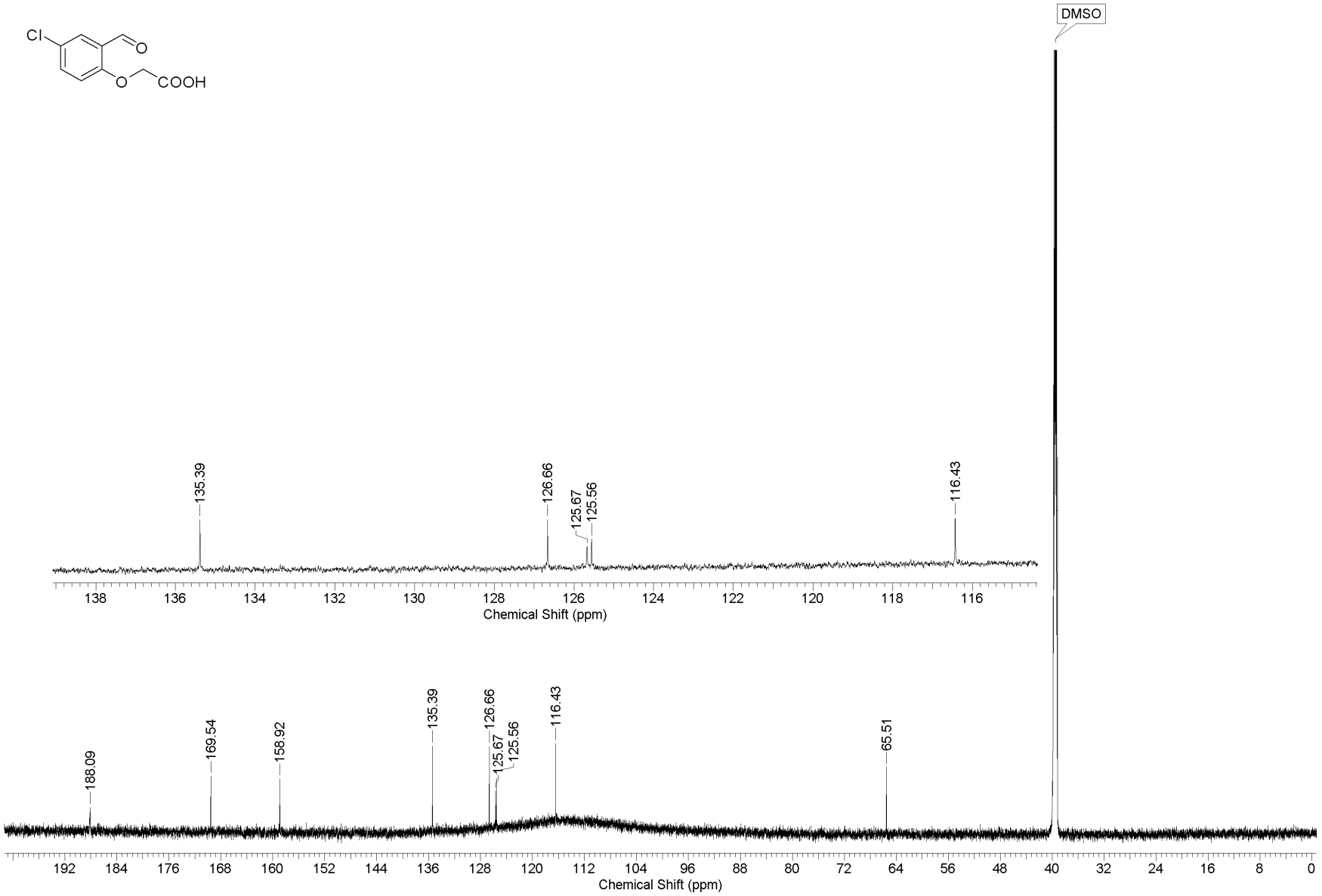

O
O
COOH
F
DMSO
7.63
7.62
7.62
7.61
7.61
7.61
7.60
7.60
7.55
7.54
7.26
7.25
7.25
7.25
7.24
7.24
4.87
1.03
1.00
1.07
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
Chemical Shift (ppm)
10.46
Water
13.12
7.63
7.62
7.61
7.61
7.55
7.54
7.25
7.25
7.25
7.24
1.03
0.95
1.00
1.07
2.02
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

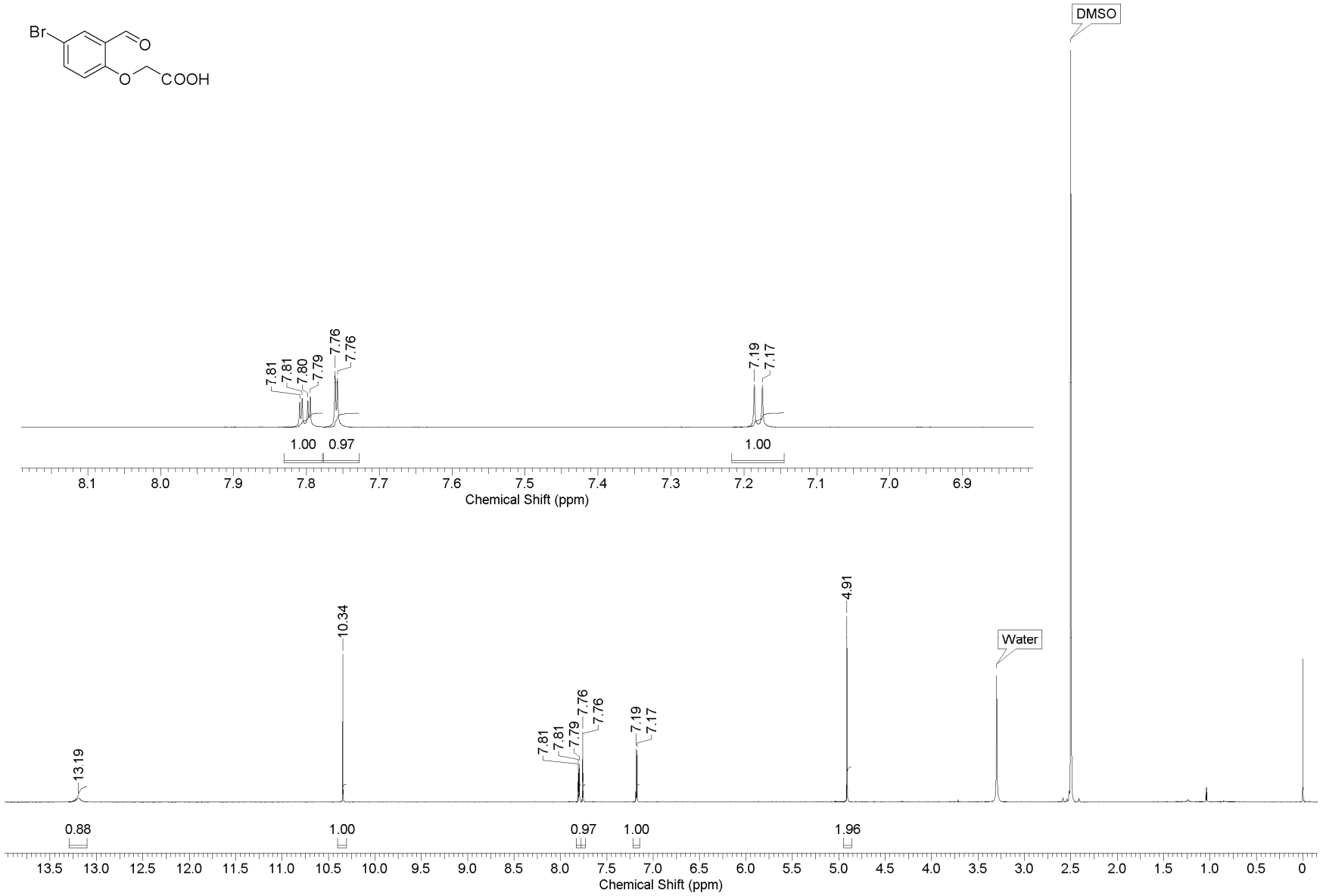

O
O
COOH
F
DMSO
189.30
189.20
170.03
154.78
153.55
147.86
Chemical Shift (ppm)
129.96
124.26
124.22
122.94
122.84
122.82
Chemical Shift (ppm)
189.30
189.20
170.03
154.78
153.55
147.86
147.81
129.96
124.22
122.94
122.84
69.59
Chemical Shift (ppm)

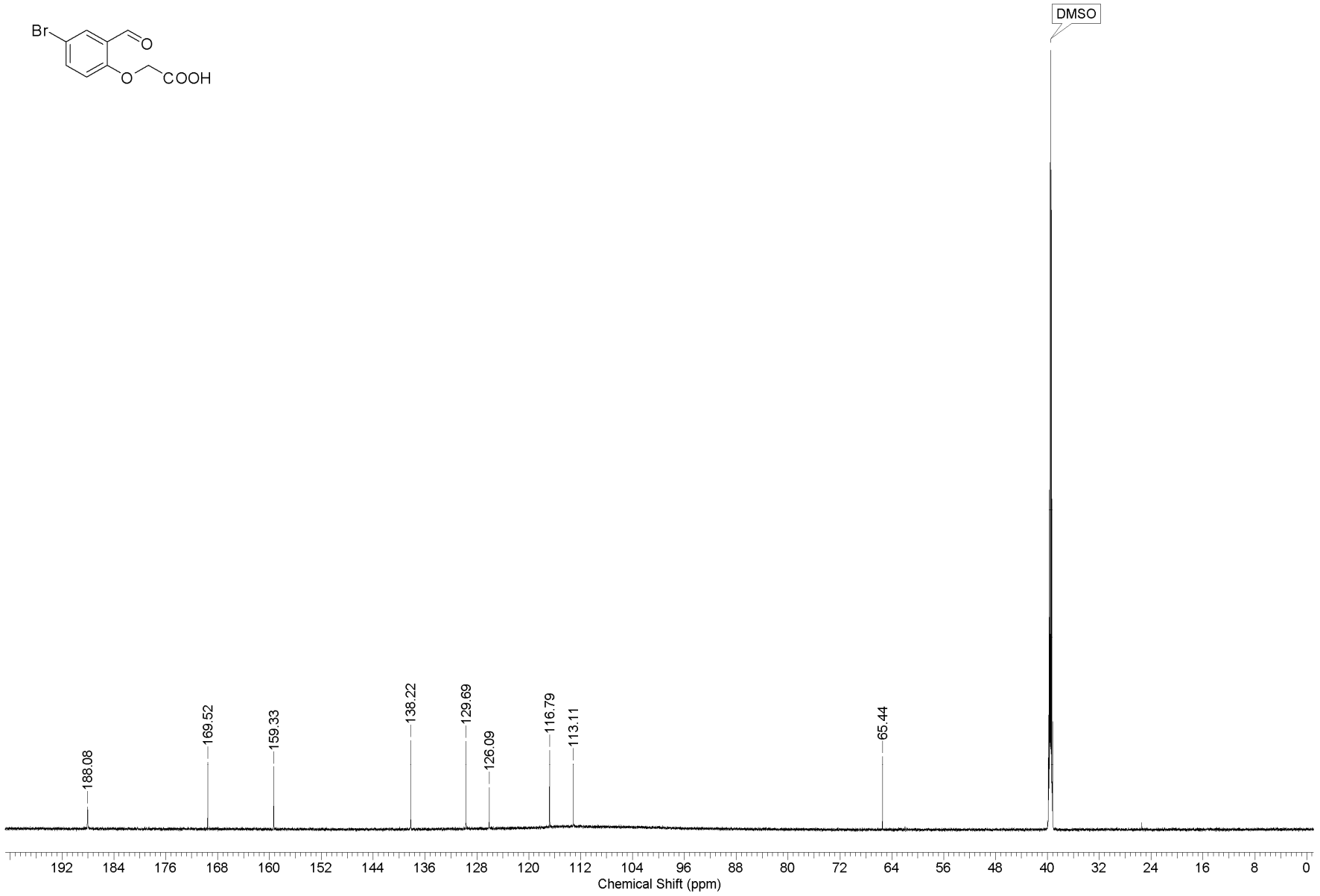

Cl
O
O
COOH
4.89
DMSO
7.55
7.56
7.54
7.16
7.15
7.15
7.14
0.98
2.04
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
Chemical Shift (ppm)
10.44
7.55
7.16
7.15
7.15
7.14
7.56
7.54
Water
13.21
0.88
0.89
0.98
2.04
2.06
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

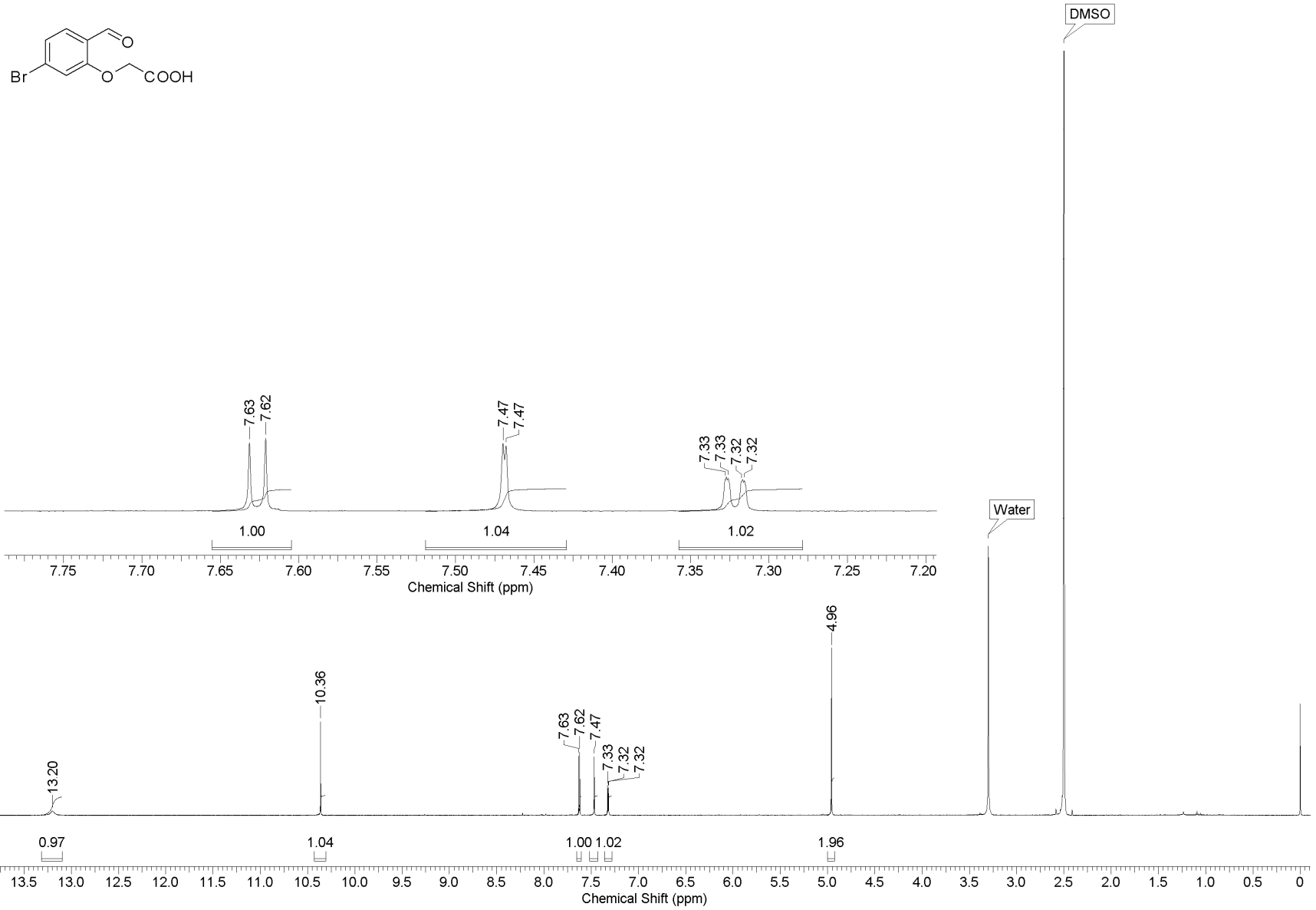

Cl
O
O
COOH
DMSO
188.83
169.53
160.86
135.06
133.11
123.51
122.32
112.79
65.58
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

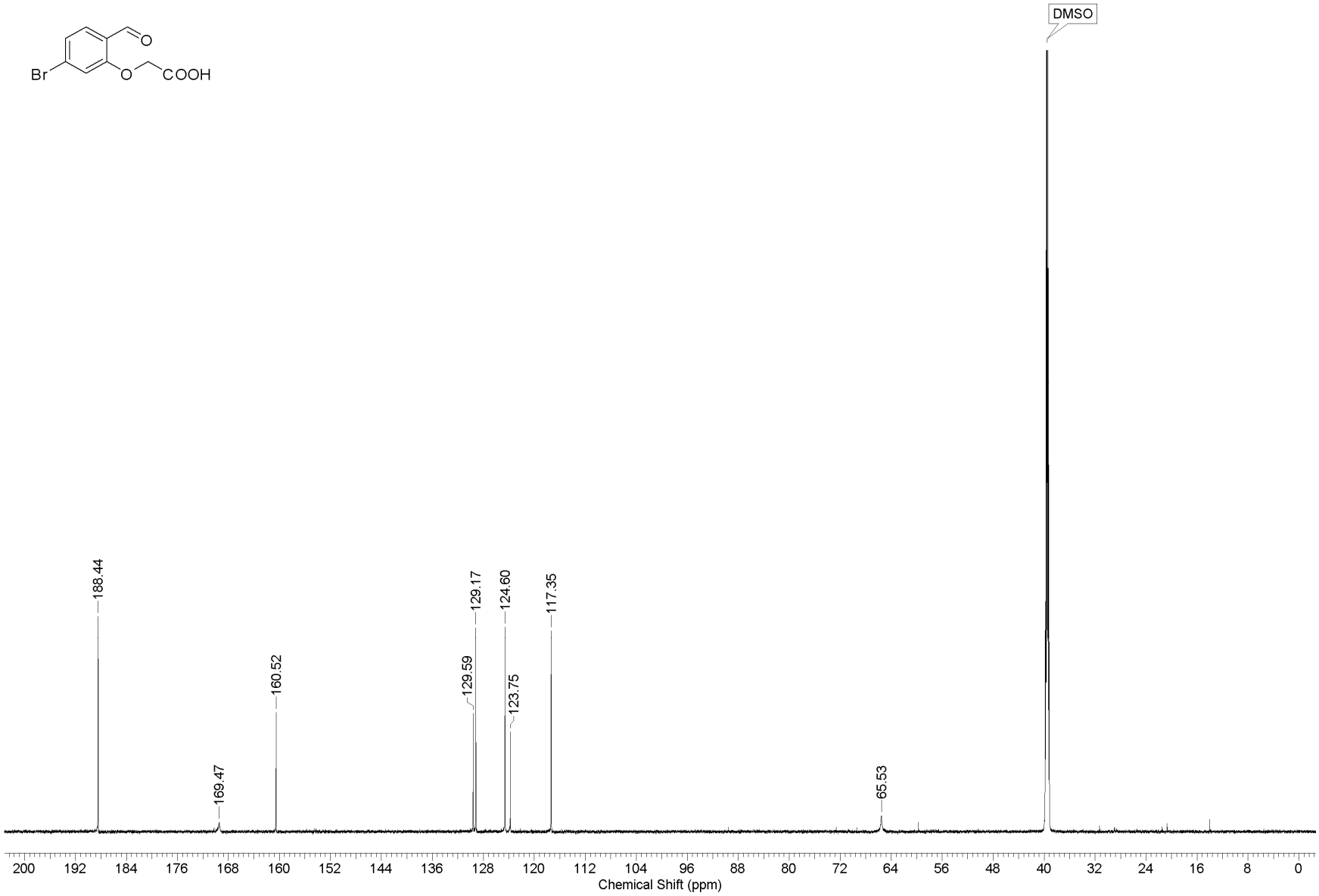

Cl
O
O
COOH
DMSO
Water
7.69
7.69
7.68
7.68
7.64
7.64
7.24
7.23
1.05
0.95
1.02
7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10
Chemical Shift (ppm)
13.22
10.36
7.69
7.68
7.64
7.24
7.23
4.92
0.87
0.96
0.95
1.02
2.10
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

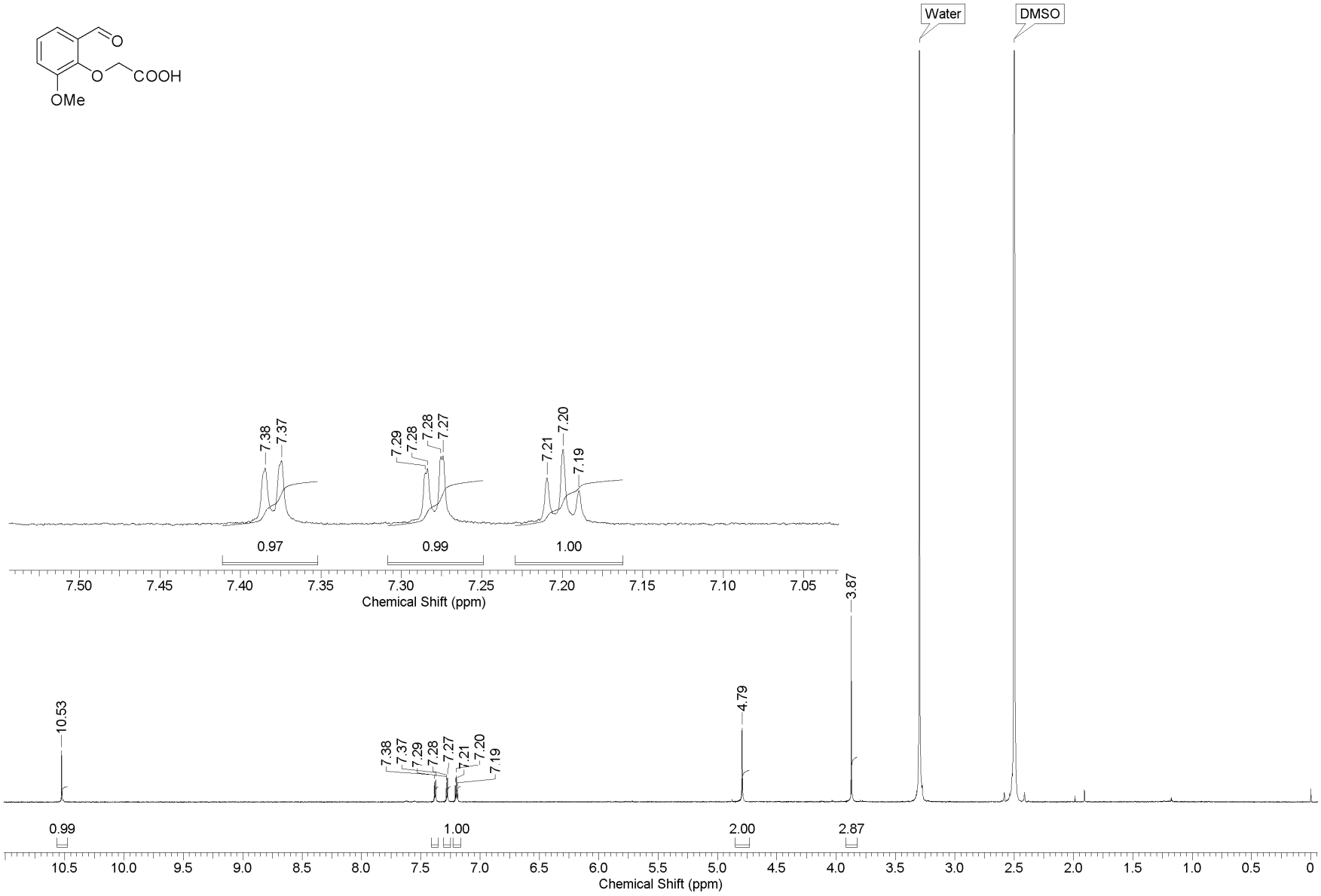

Cl
O
O
COOH
DMSO
135.39
126.66
125.67
125.56
116.43
138
136
134
132
130
128
126
124
122
120
118
116
Chemical Shift (ppm)
188.09
169.54
158.92
135.39
126.66
125.67
125.56
116.43
65.51
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

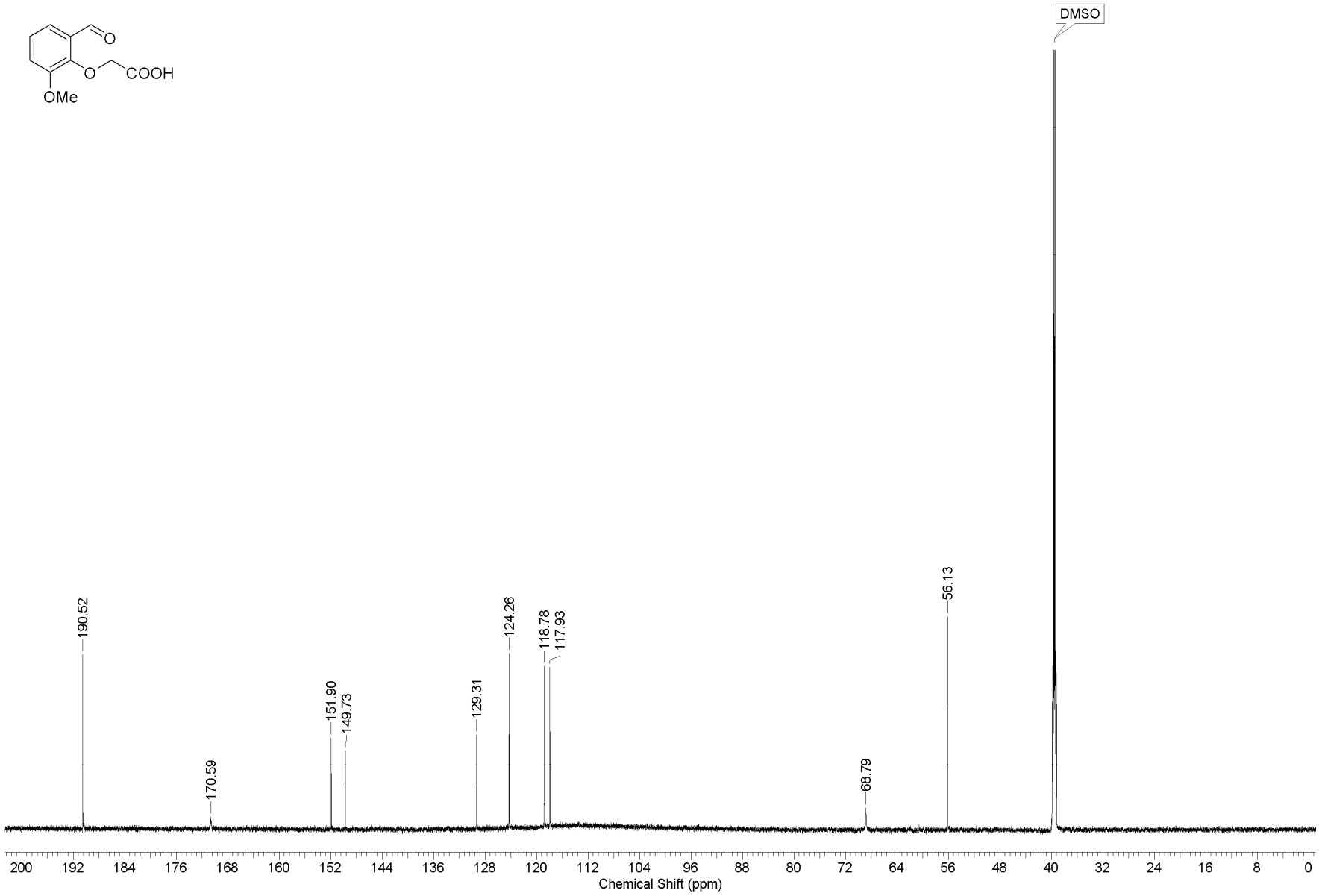

Br
O
O
COOH
DMSO
7.81
7.81
7.80
7.79
7.76
7.76
7.19
7.17
1.00
0.97
1.00
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
Chemical Shift (ppm)
13.19
10.34
4.91
Water
7.81
7.81
7.79
7.76
7.76
7.19
7.17
0.88
1.00
0.97
1.00
1.96
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

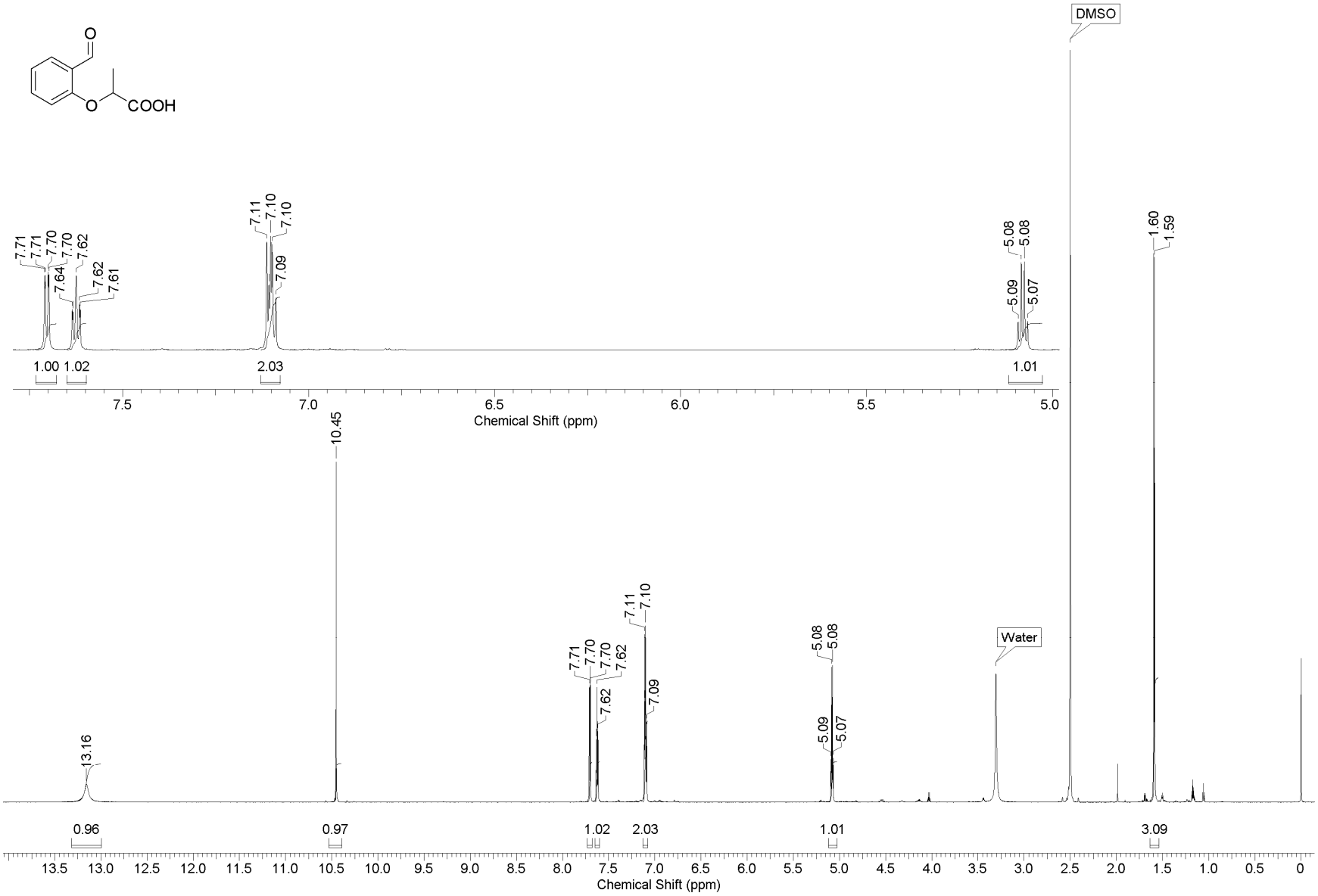

Br
O
O
COOH
DMSO
188.08
169.52
159.33
138.22
129.69
126.09
116.79
113.11
65.44
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

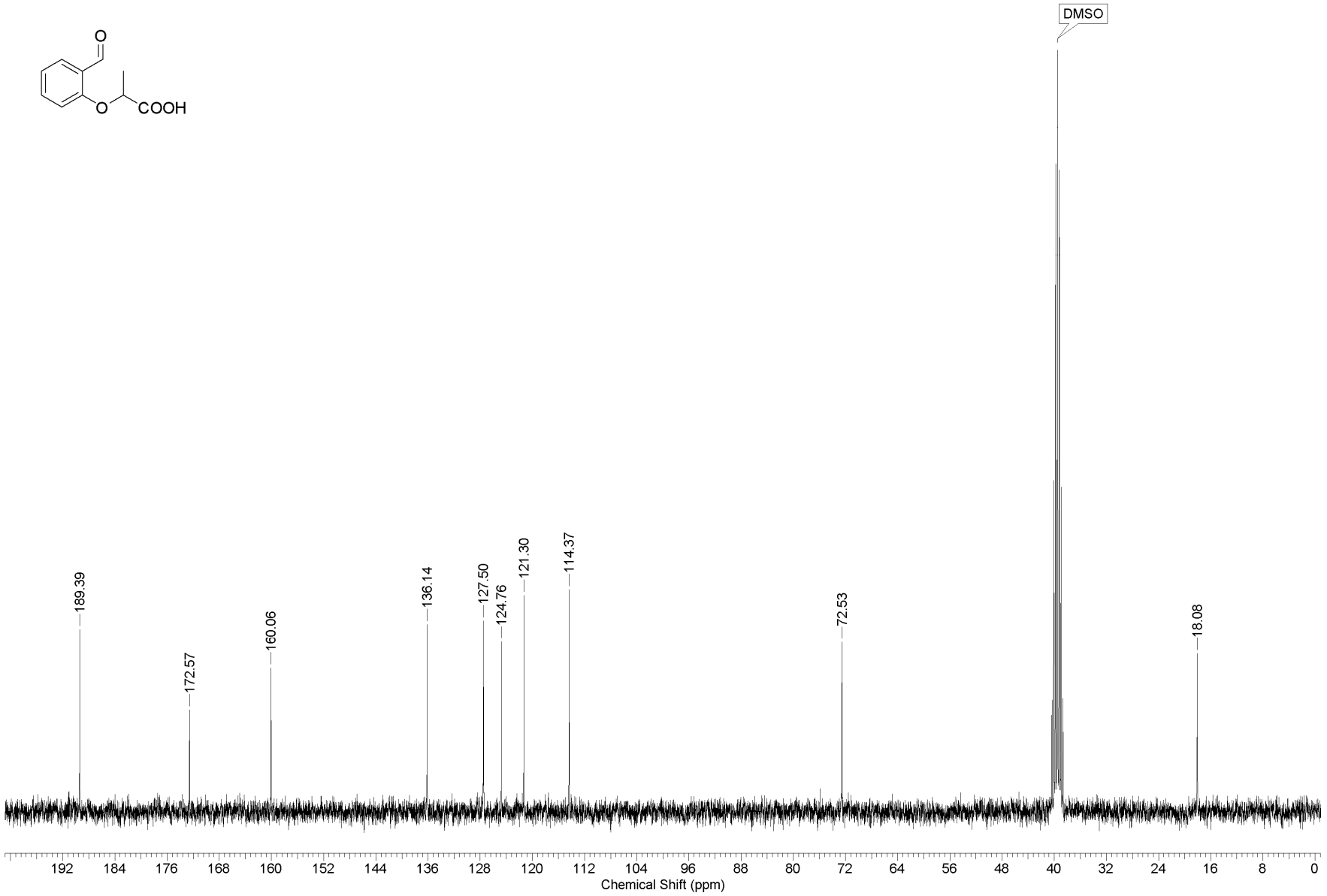

Br
O
O
COOH
DMSO
Water
7.63
7.62
7.47
7.47
7.33
7.33
7.32
7.32
1.00
1.04
1.02
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20
Chemical Shift (ppm)
13.20
10.36
7.63
7.62
7.47
7.33
7.32
7.32
4.96
0.97
1.04
1.00
1.02
1.96
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

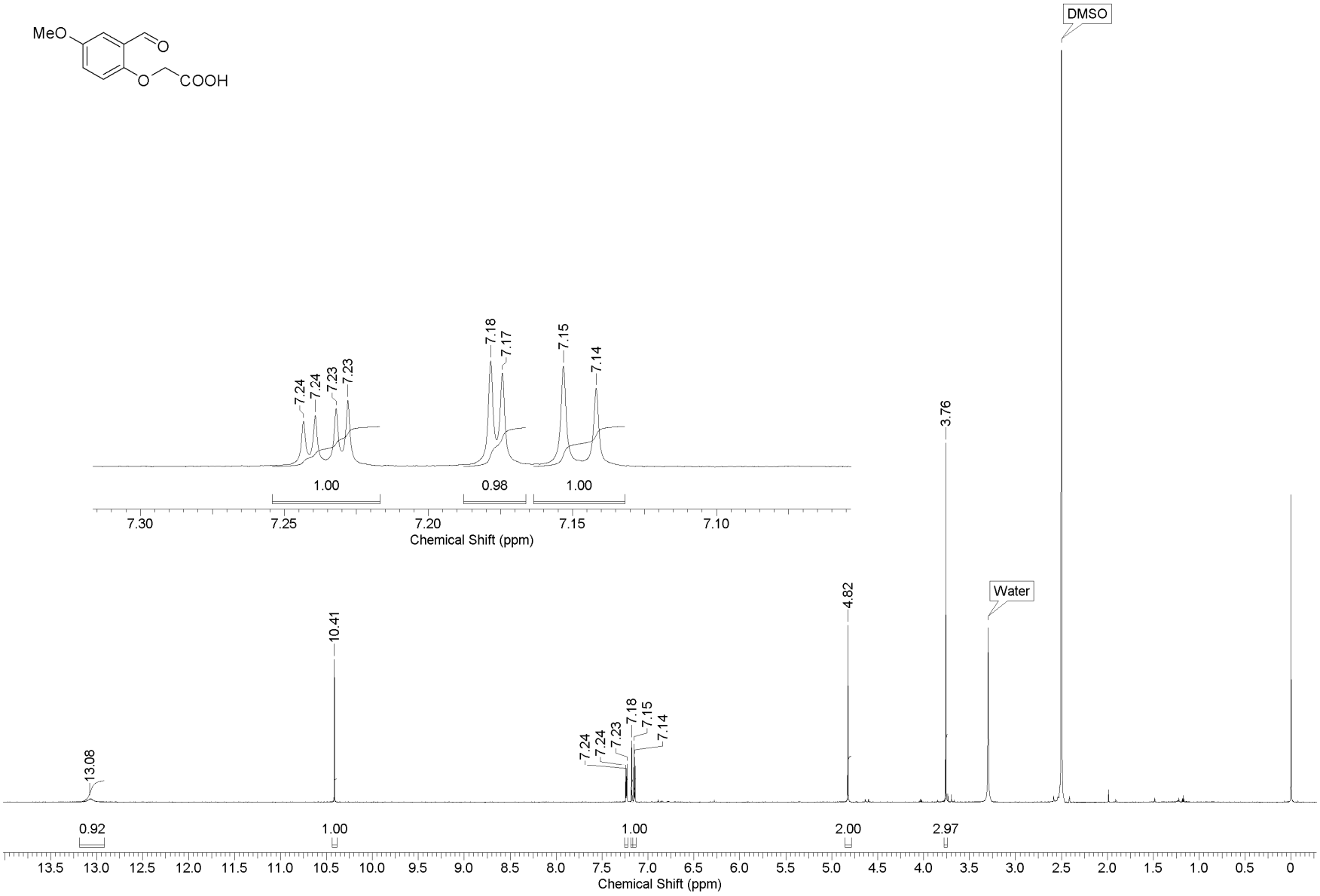

Br
O
O
COOH
DMSO
188.44
169.47
160.52
129.59
129.17
124.60
123.75
117.35
65.53
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

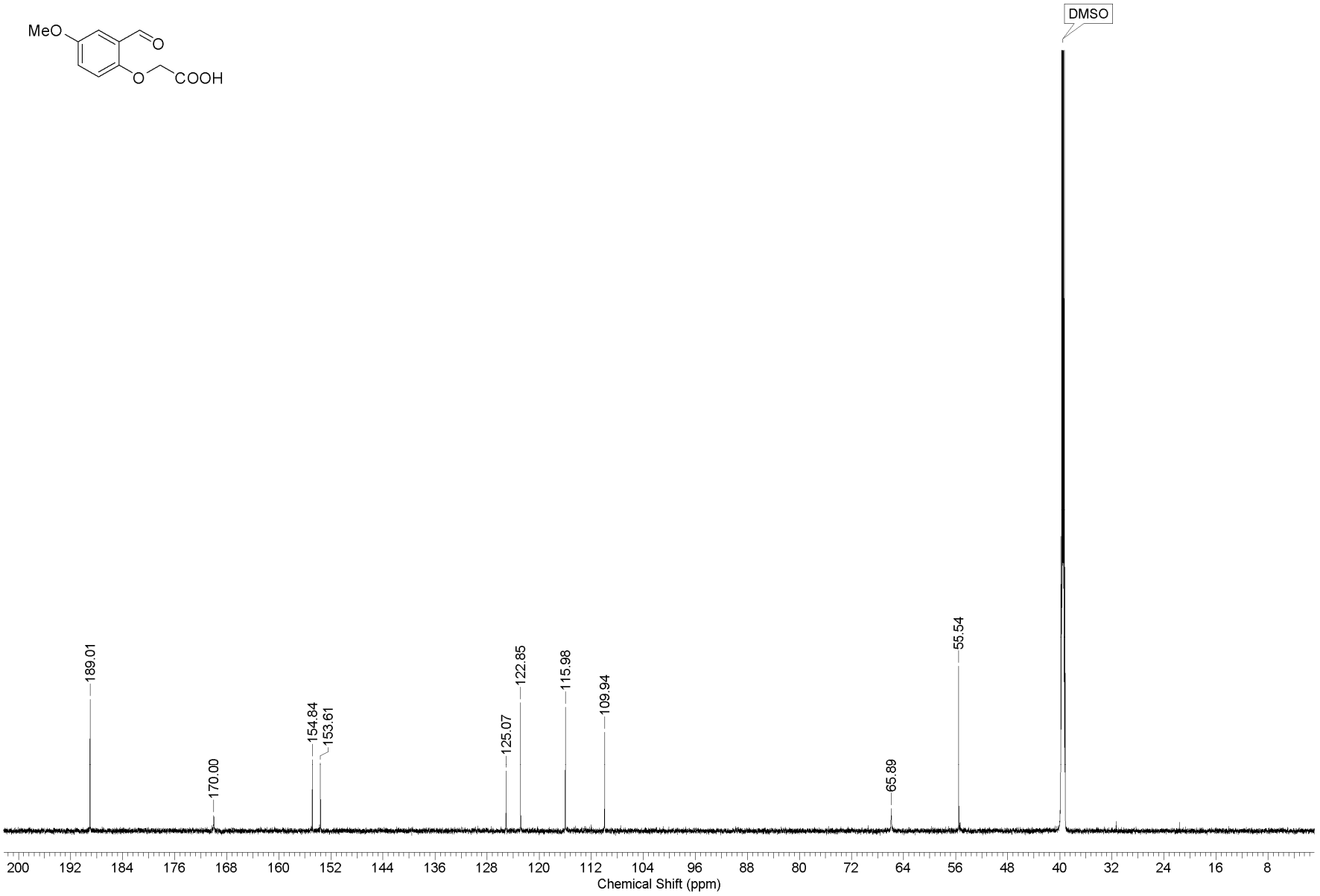

O
O
COOH
OMe
Water
DMSO
7.38
7.37
7.29
7.28
7.28
7.27
7.21
7.20
7.19
0.97
0.99
1.00
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
Chemical Shift (ppm)
3.87
10.53
4.79
7.38
7.37
7.29
7.28
7.27
7.21
7.20
7.19
0.99
1.00
2.00
2.87
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

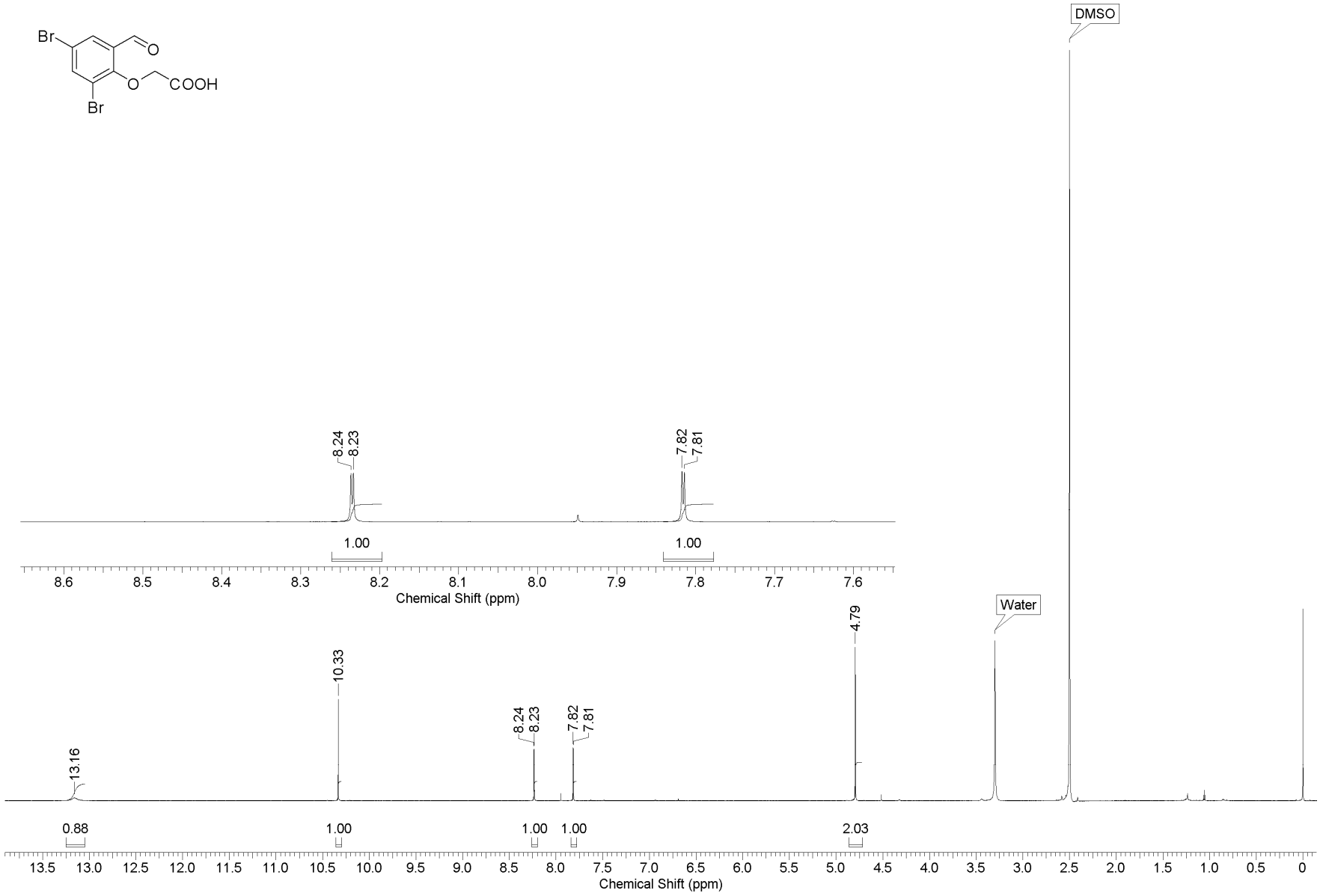

O
O
COOH
OMe
DMSO
190.52
170.59
151.90
149.73
129.31
124.26
118.78
117.93
68.79
56.13
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

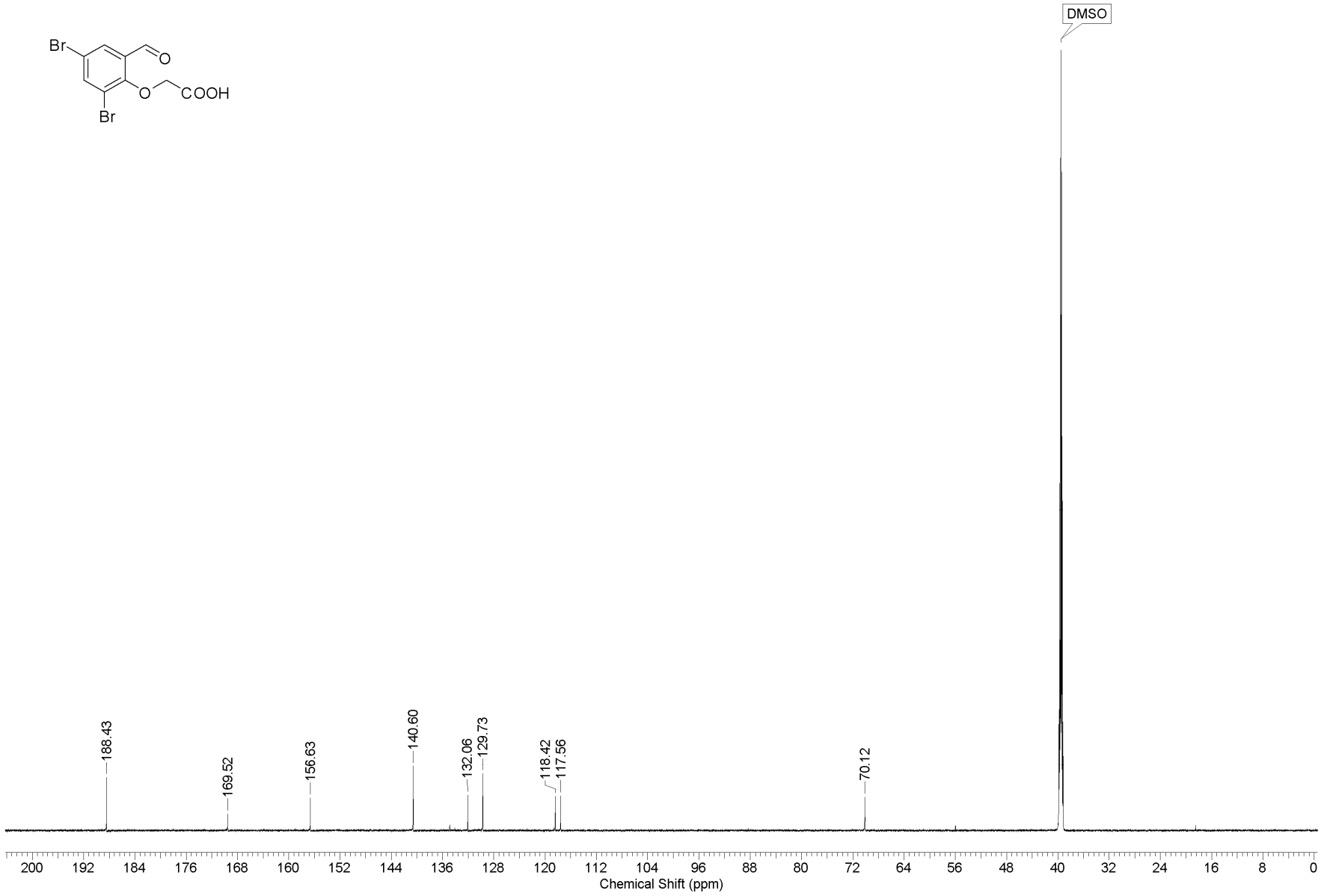

O
O
COOH
DMSO
Water
7.71
7.71
7.70
7.70
7.64
7.62
7.62
7.61
7.11
7.10
7.10
7.09
5.08
5.08
5.09
5.07
1.60
1.59
1.00
1.02
2.03
1.01
Chemical Shift (ppm)
10.45
13.16
0.96
0.97
1.02
2.03
1.01
3.09
Chemical Shift (ppm)

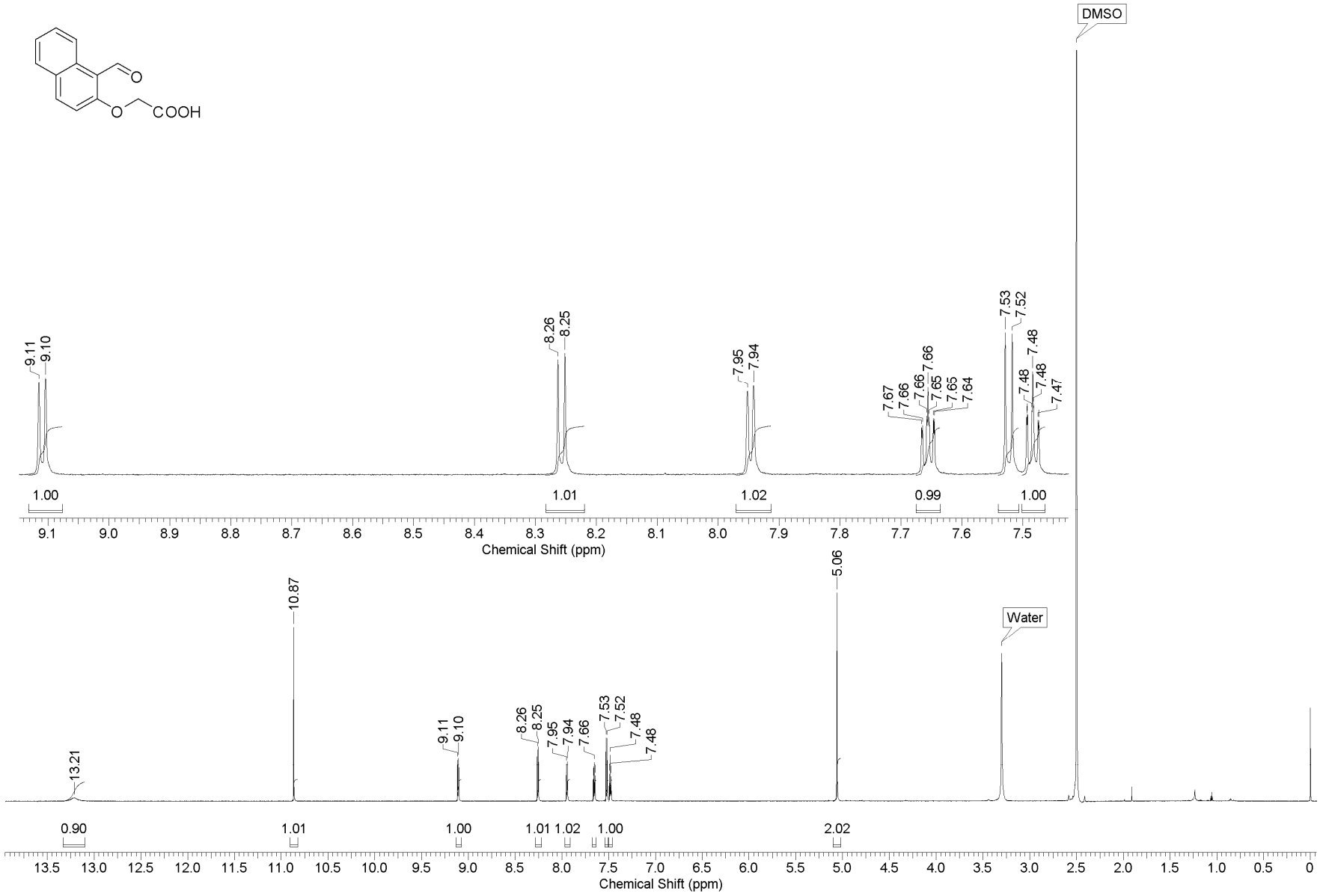

O
O
COOH
DMSO
189.39
172.57
160.06
136.14
127.50
124.76
121.30
114.37
72.53
18.08
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

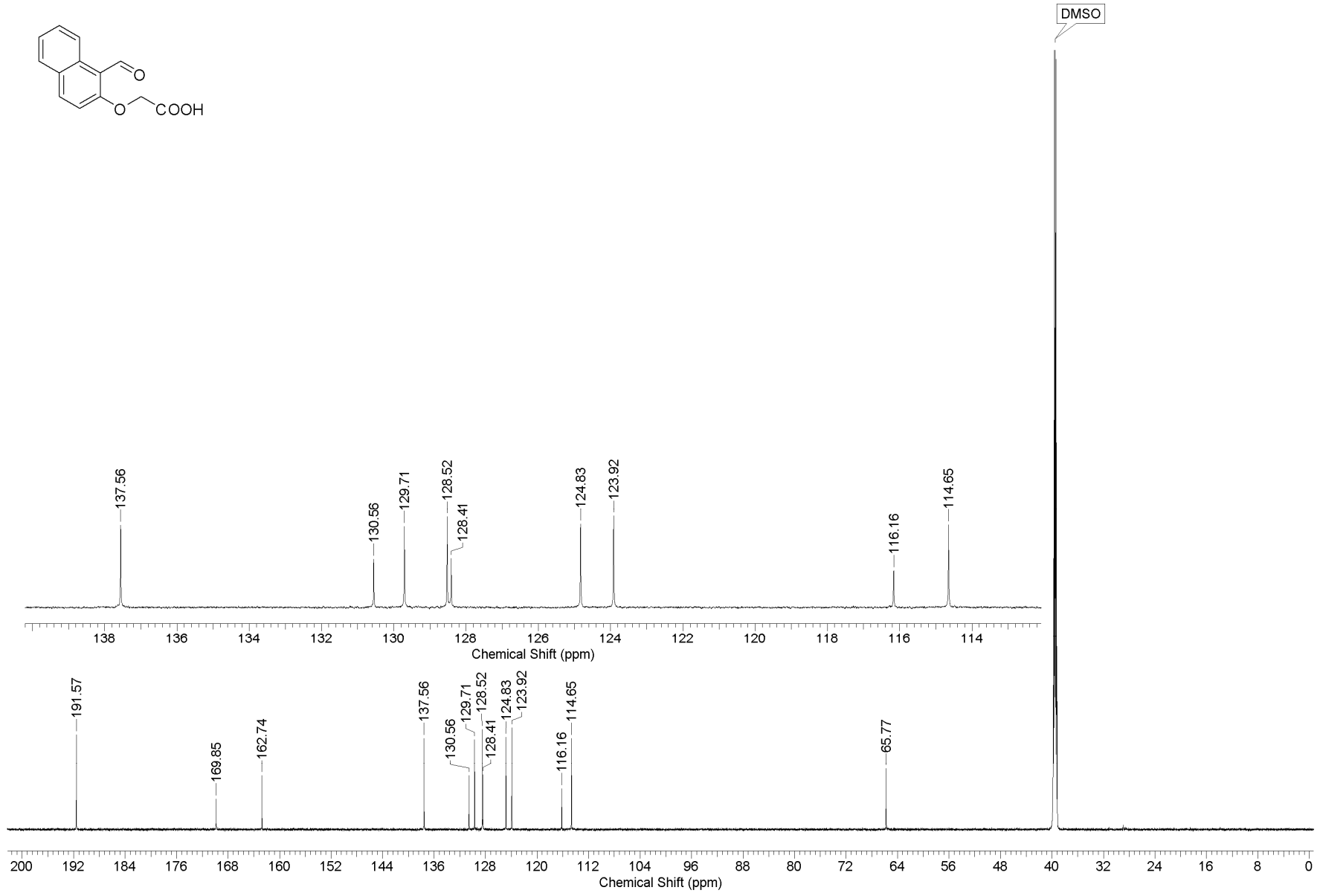

MeO
O
O
COOH
DMSO
Water
13.08
10.41
7.24
7.24
7.23
7.23
7.18
7.17
7.15
7.14
4.82
3.76
0.92
1.00
1.00
2.00
2.97
1.00
0.98
1.00
Chemical Shift (ppm)
Chemical Shift (ppm)

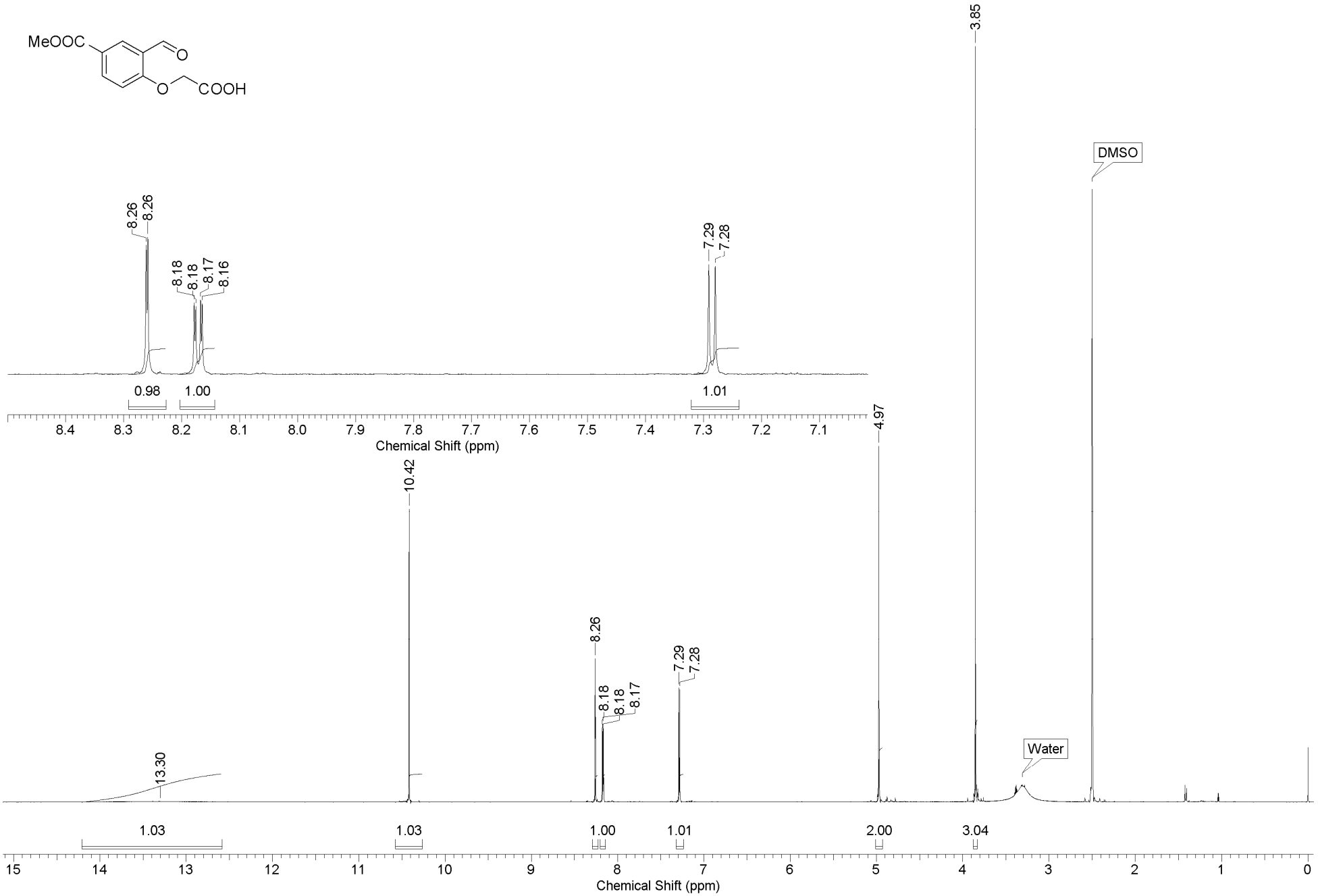

MeO
O
O
COOH
DMSO
189.01
170.00
154.84
153.61
125.07
122.85
115.98
109.94
65.89
55.54
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)

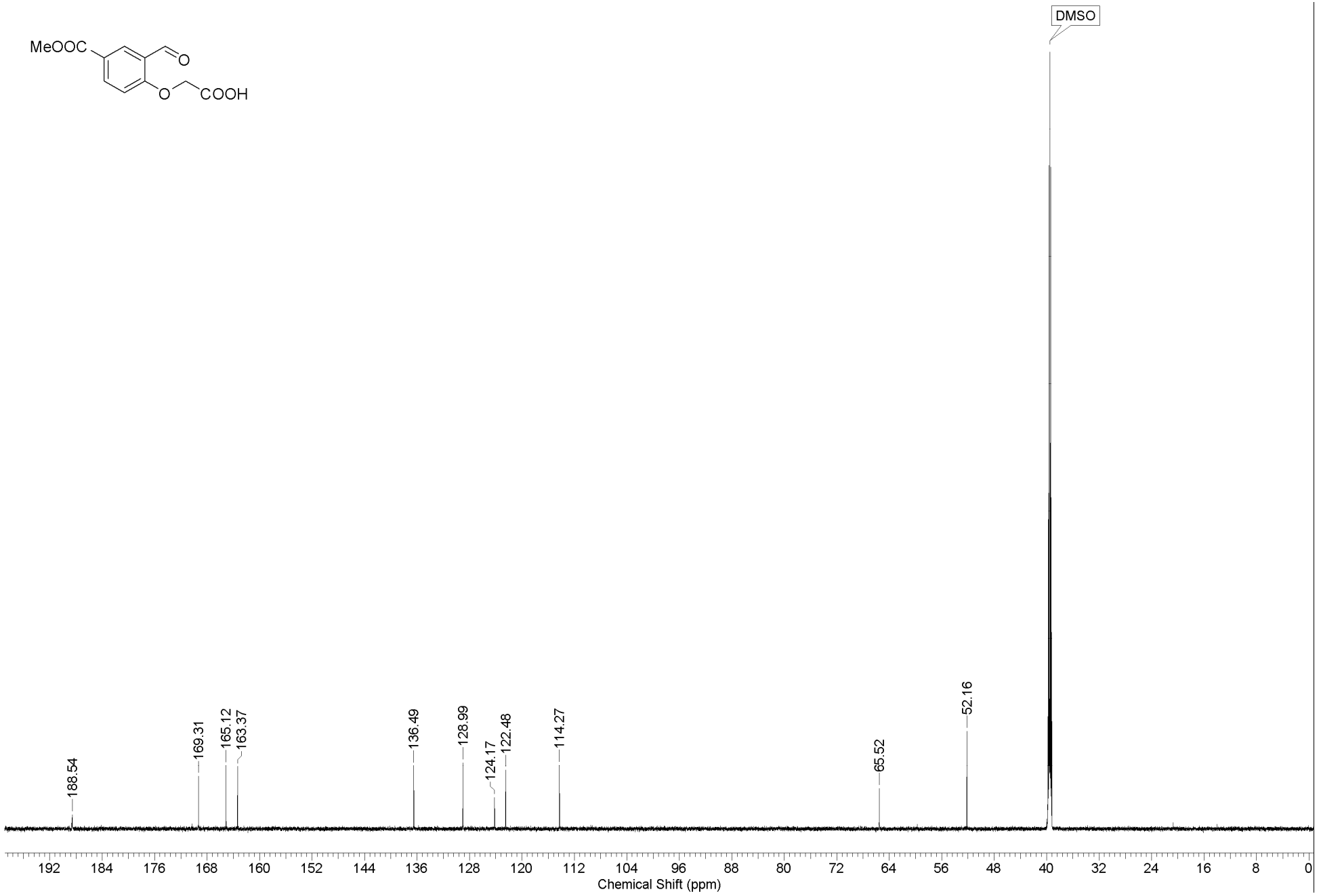

Br
O
O
COOH
Br
DMSO
8.24
8.23
7.82
7.81
1.00
1.00
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
Chemical Shift (ppm)
Water
4.79
10.33
13.16
0.88
1.00
1.00
1.00
2.03
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

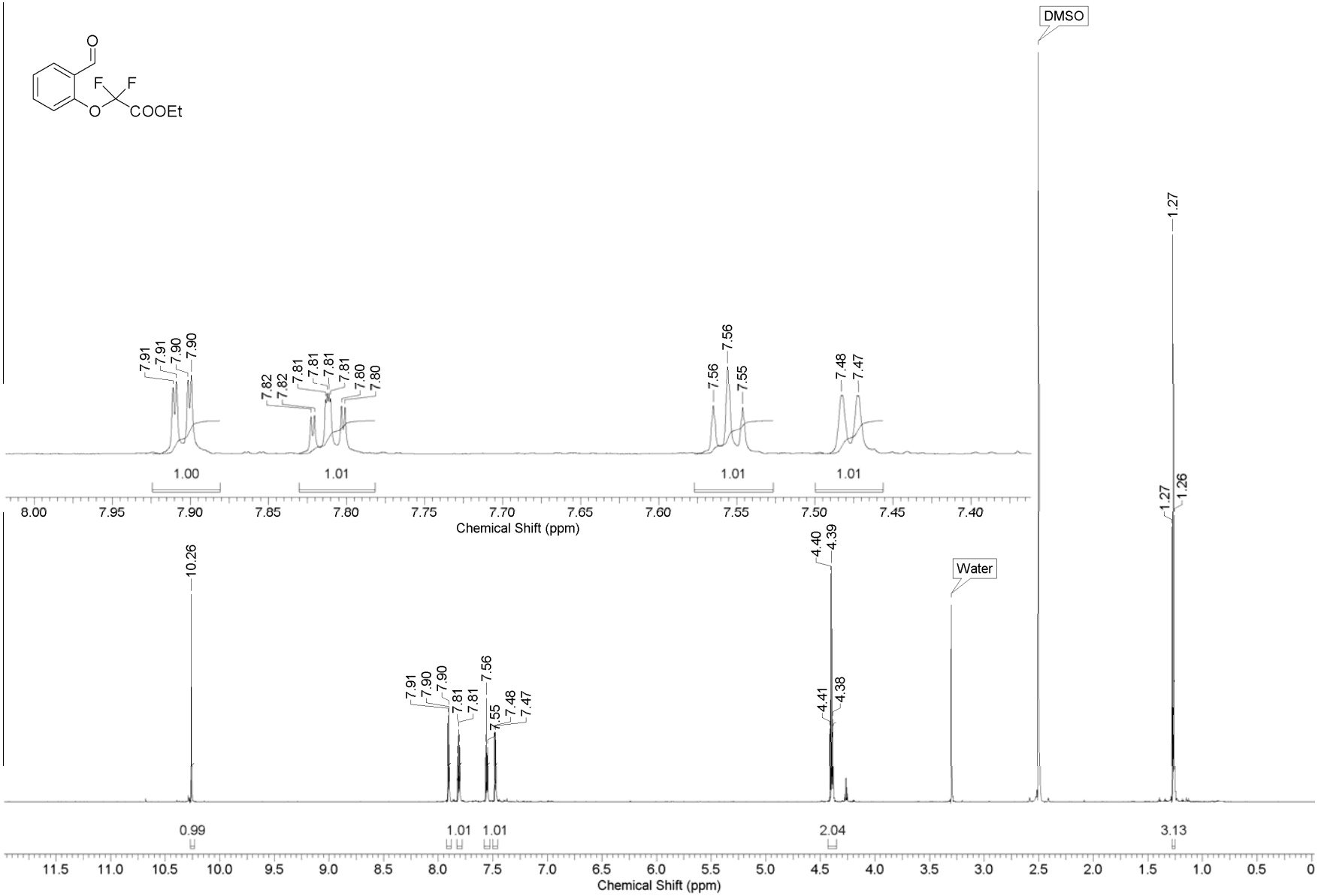

Br
O
O
COOH
Br
DMSO
188.43
169.52
156.63
140.60
132.06
129.73
118.42
117.56
70.12
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

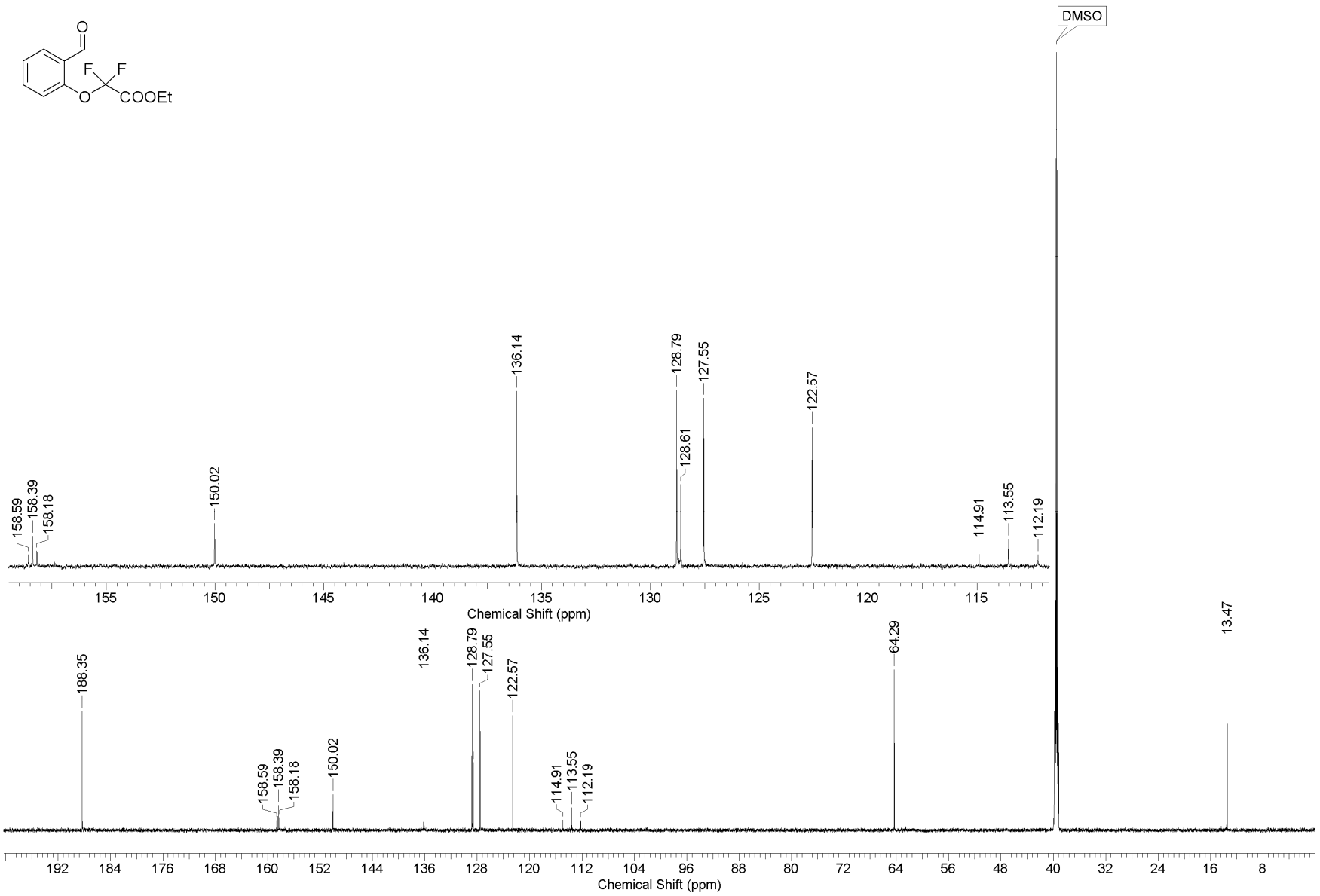

O
O
COOH
DMSO
9.11
9.10
8.26
8.25
7.95
7.94
7.67
7.66
7.66
7.66
7.65
7.65
7.64
7.53
7.52
7.48
7.48
7.48
7.47
1.00
1.01
1.02
0.99
1.00
Chemical Shift (ppm)
10.87
5.06
Water
13.21
9.11
9.10
8.26
8.25
7.95
7.94
7.66
7.53
7.52
7.48
7.48
0.90
1.01
1.00
1.01
1.02
1.00
2.02
Chemical Shift (ppm)

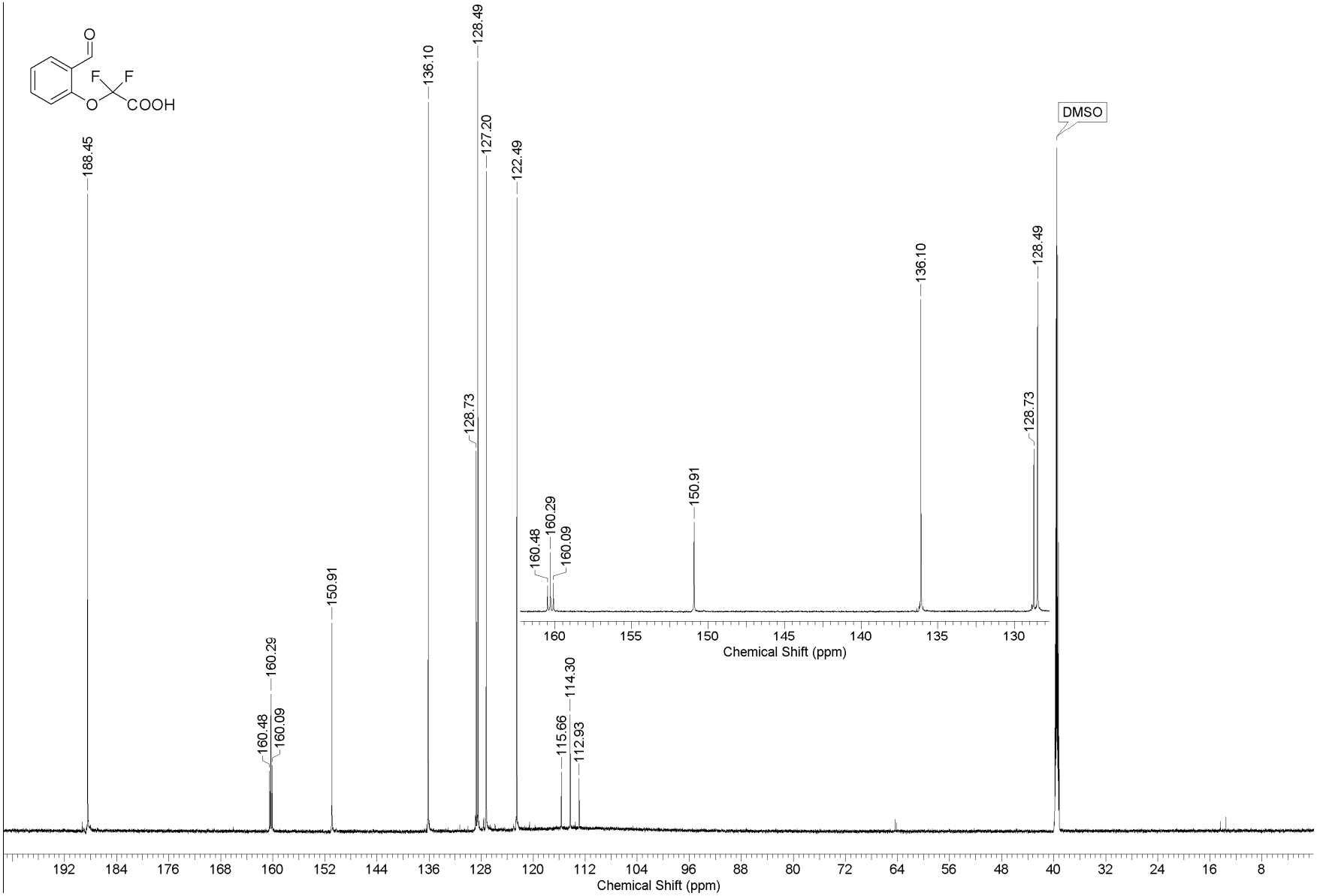

O
O
COOH
DMSO
137.56
130.56
129.71
128.52
128.41
124.83
123.92
116.16
114.65
138
136
134
132
130
128
126
124
122
120
118
116
114
Chemical Shift (ppm)
191.57
169.85
162.74
137.56
130.56
129.71
128.52
128.41
124.83
123.92
116.16
114.65
65.77
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

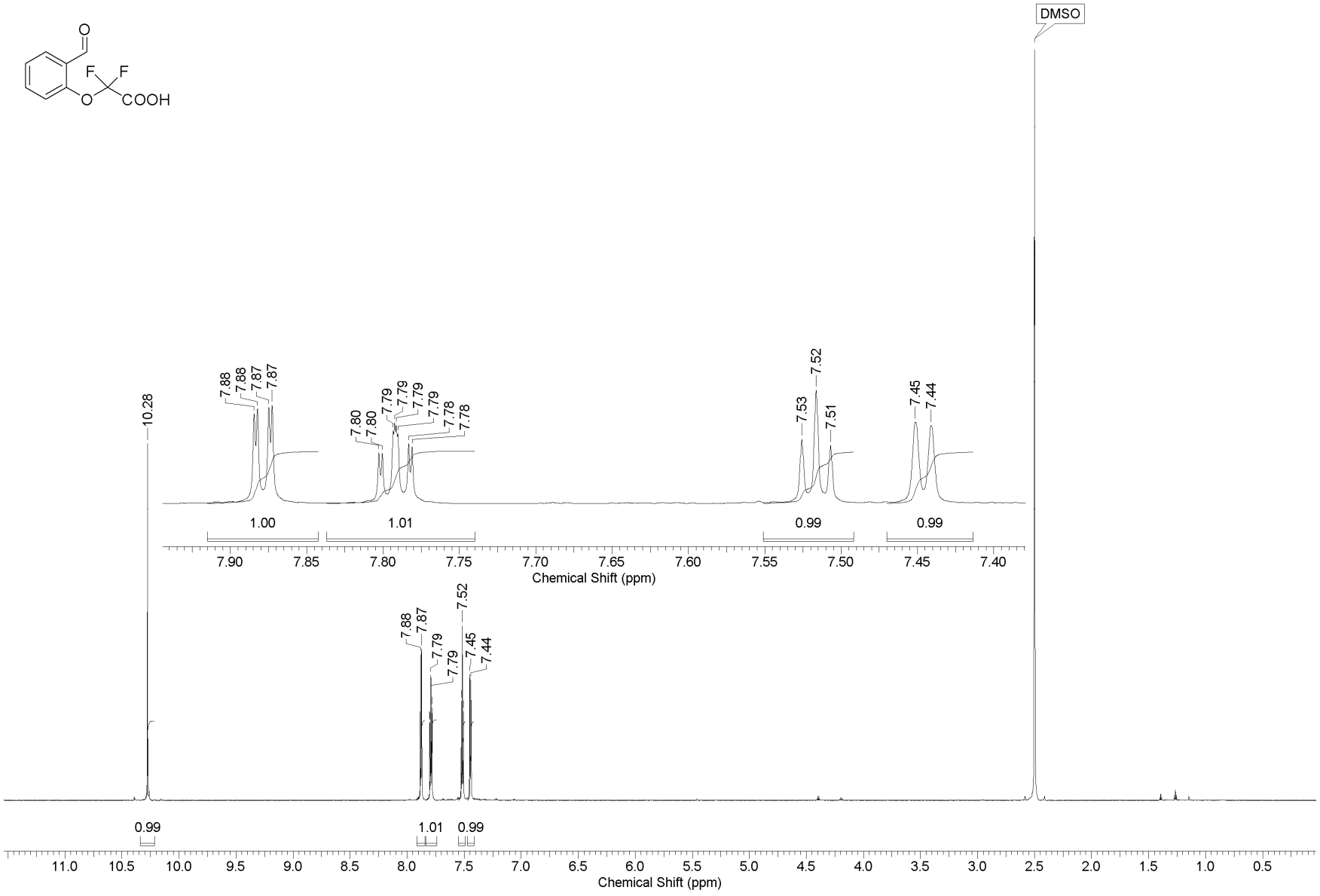

MeOOC
O
O
COOH
3.85
DMSO
8.26
8.26
8.18
8.18
8.17
8.16
7.29
7.28
0.98
1.00
1.01
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
Chemical Shift (ppm)
4.97
10.42
8.26
8.18
8.18
8.17
7.29
7.28
13.30
Water
1.03
1.03
1.00
1.01
2.00
3.04
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

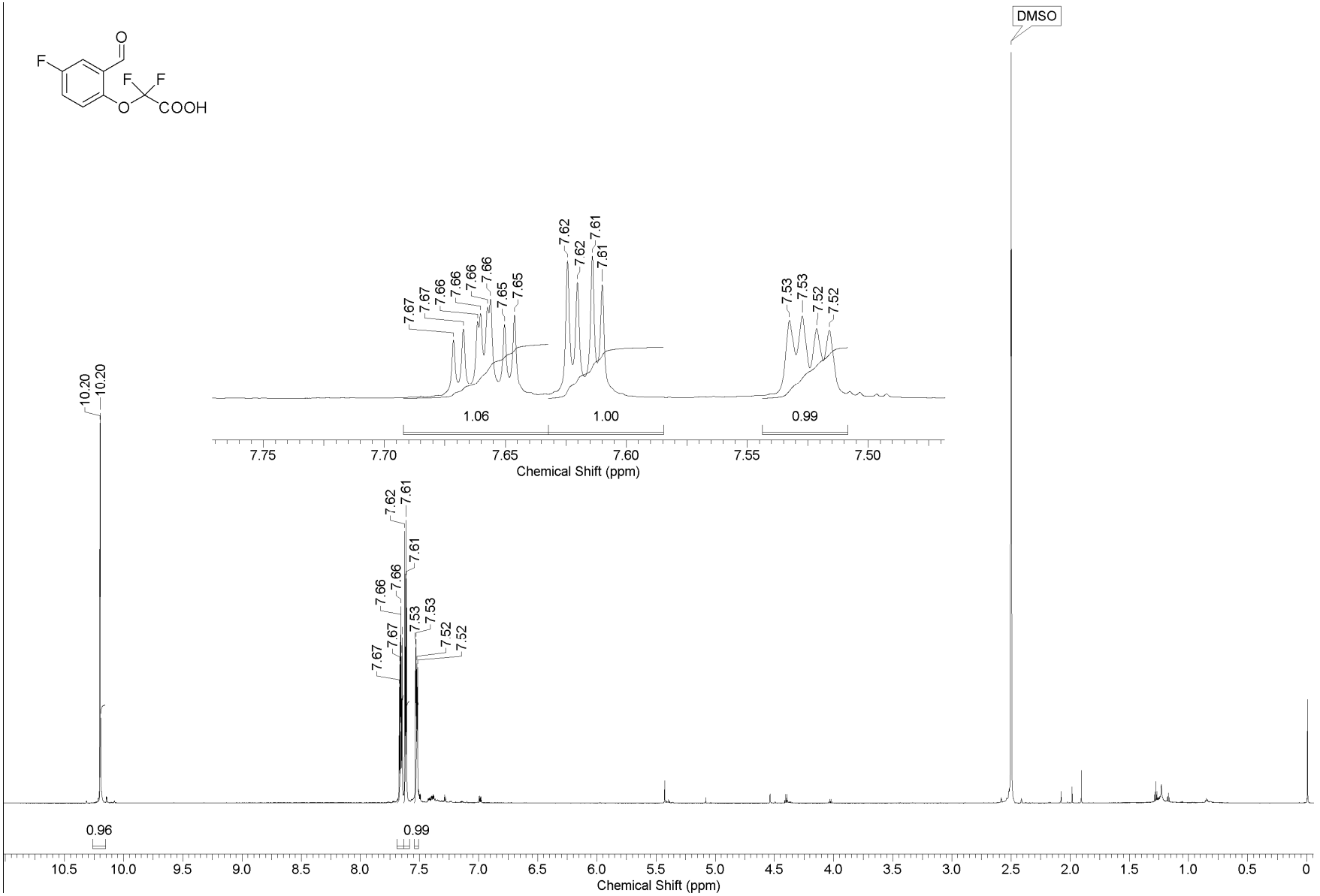

MeOOC
O
O
COOH
DMSO
188.54
169.31
165.12
163.37
136.49
128.99
124.17
122.48
114.27
65.52
52.16
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

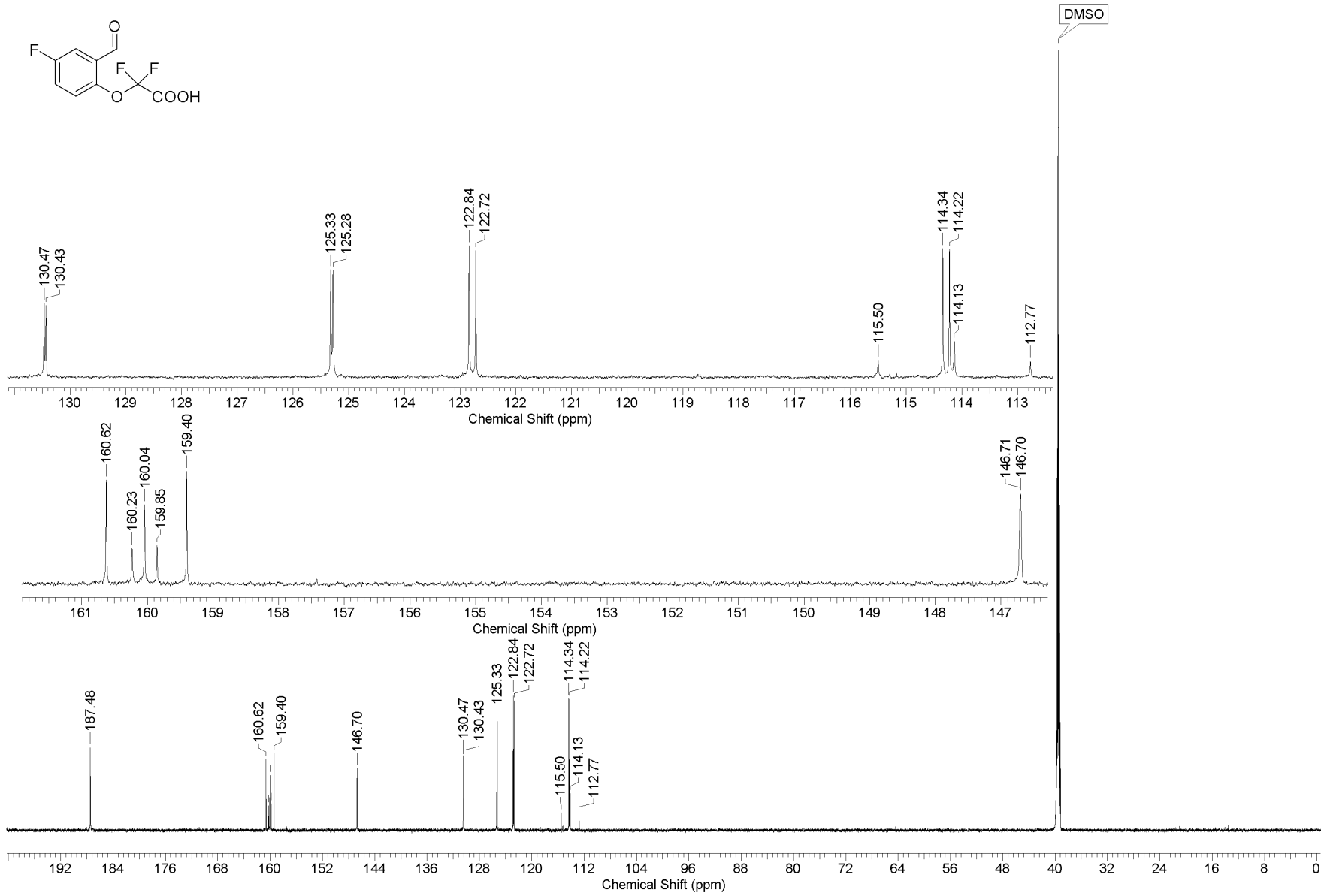

O
F
F
O
COOEt
DMSO
Water
7.91
7.91
7.90
7.90
7.82
7.82
7.81
7.81
7.81
7.80
7.80
7.56
7.56
7.55
7.48
7.47
1.00
1.01
1.01
1.01
8.00
7.95
7.90
7.85
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
Chemical Shift (ppm)
10.26
4.40
4.39
1.27
1.26
7.91
7.90
7.90
7.81
7.81
7.56
7.55
7.48
7.47
4.41
4.38
0.99
1.01
1.01
2.04
3.13
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

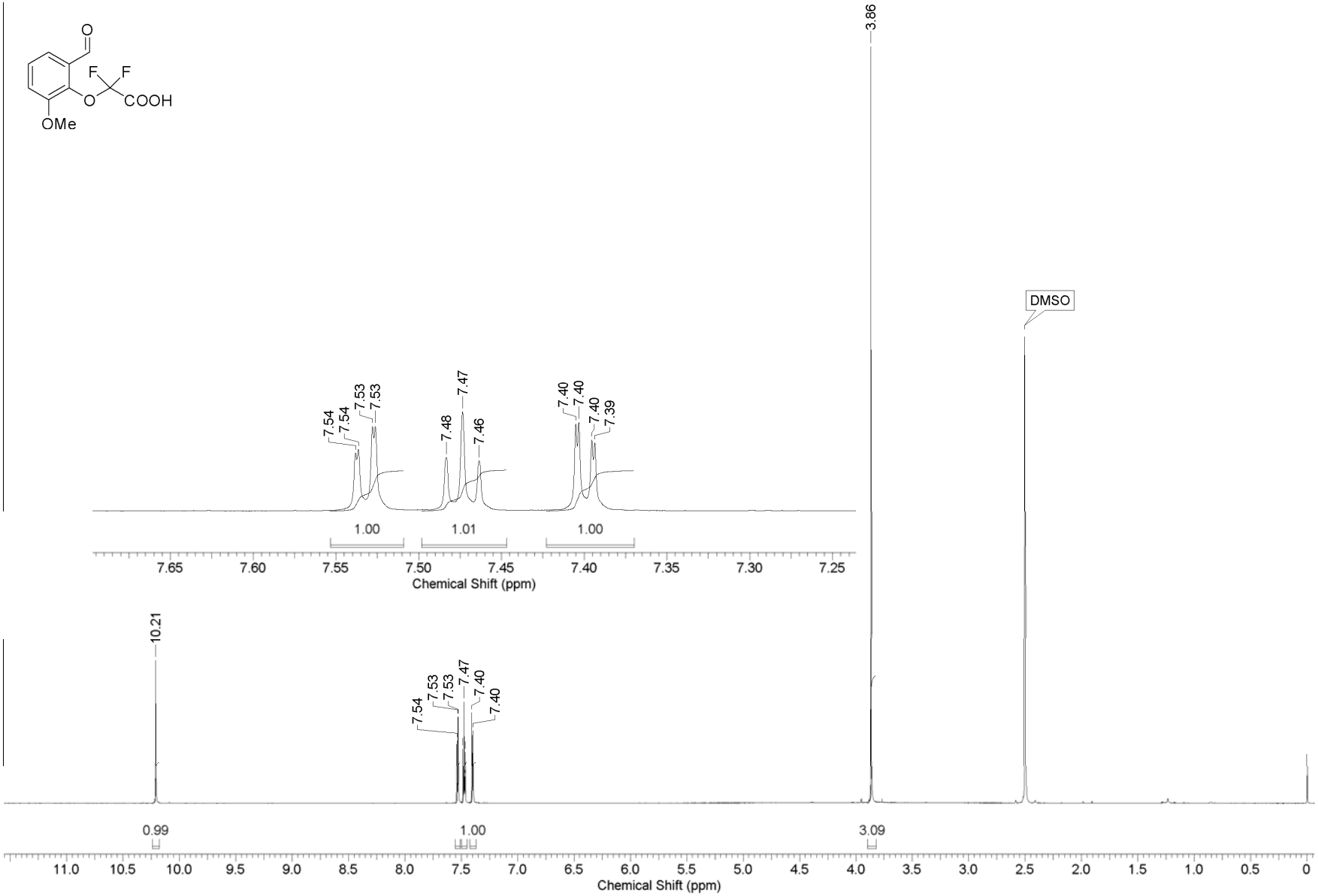

O
F
F
O
COOEt
DMSO
158.59
158.39
158.18
150.02
136.14
128.79
128.61
127.55
122.57
114.91
113.55
112.19
155
150
145
140
135
130
125
120
115
Chemical Shift (ppm)
188.35
158.59
158.39
158.18
150.02
136.14
128.79
127.55
122.57
114.91
113.55
112.19
64.29
13.47
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

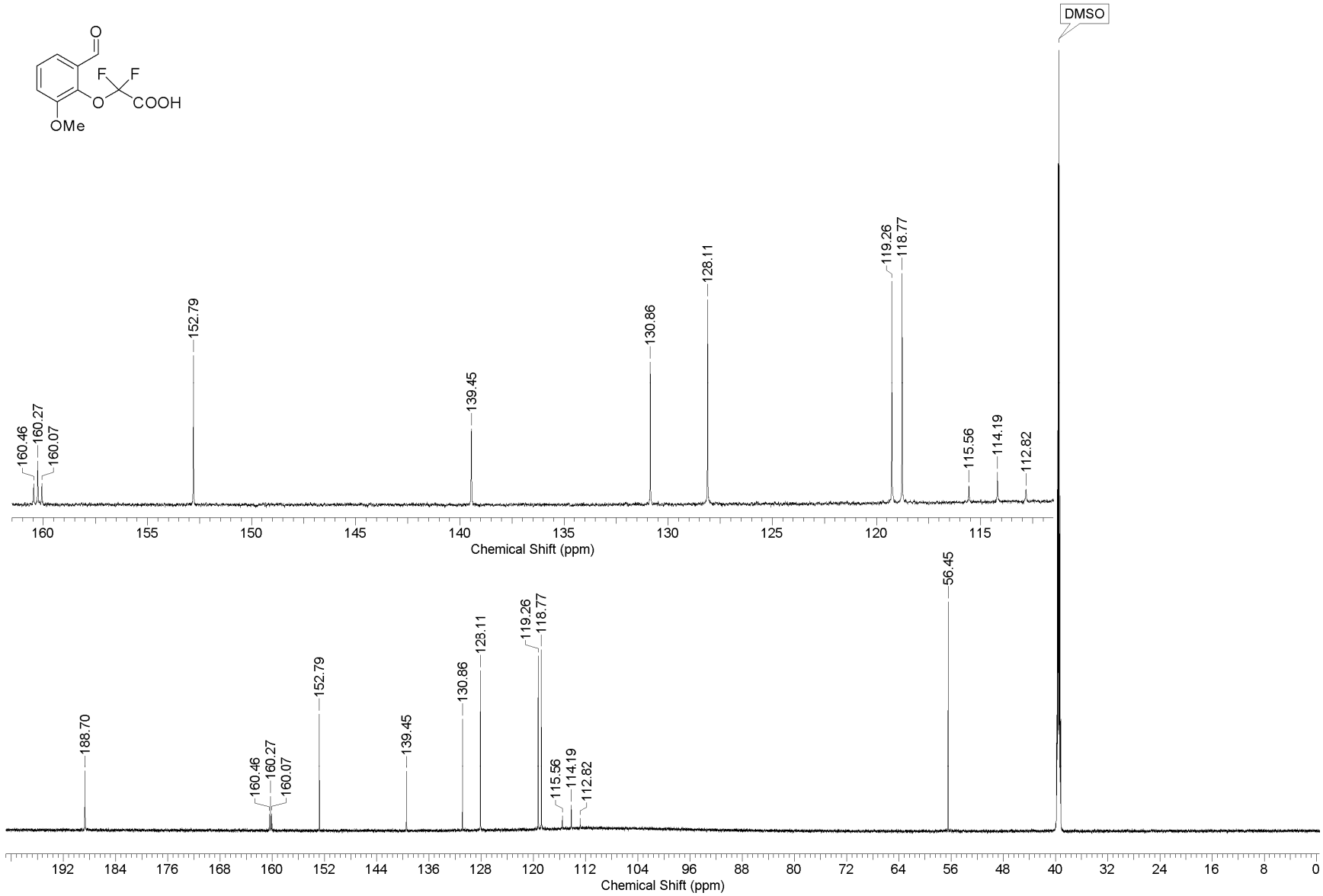

O
F
F
O
COOH
188.45
160.48
160.29
160.09
150.91
136.10
128.73
128.49
127.20
122.49
115.66
114.30
112.93
DMSO
Chemical Shift (ppm)
Chemical Shift (ppm)

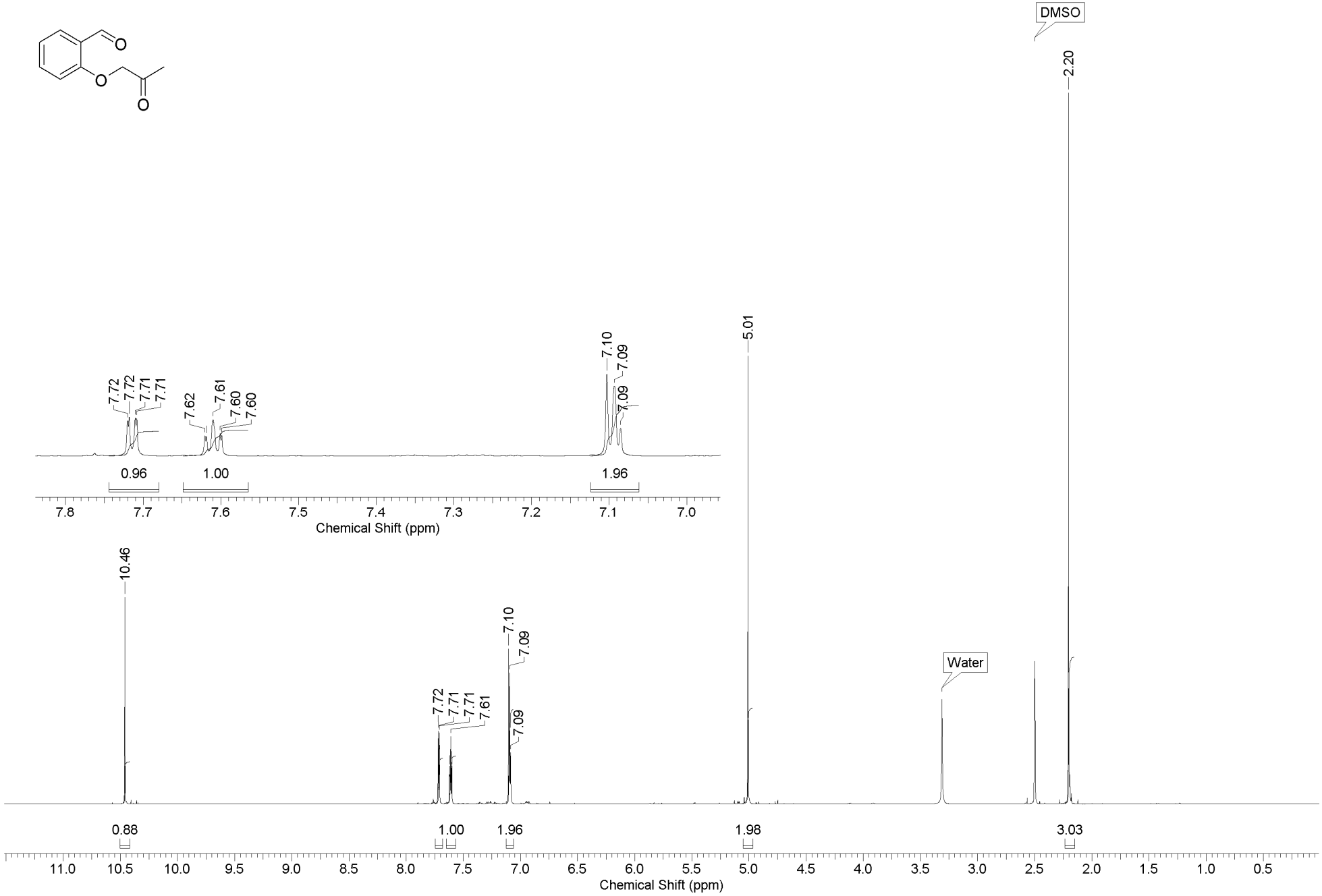

O
F
F
O
COOH
DMSO
10.28
7.88
7.88
7.87
7.87
7.80
7.80
7.79
7.79
7.79
7.79
7.78
7.78
7.53
7.52
7.51
7.45
7.44
1.00
1.01
0.99
0.99
7.90
7.85
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
Chemical Shift (ppm)
0.99
1.01
0.99
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

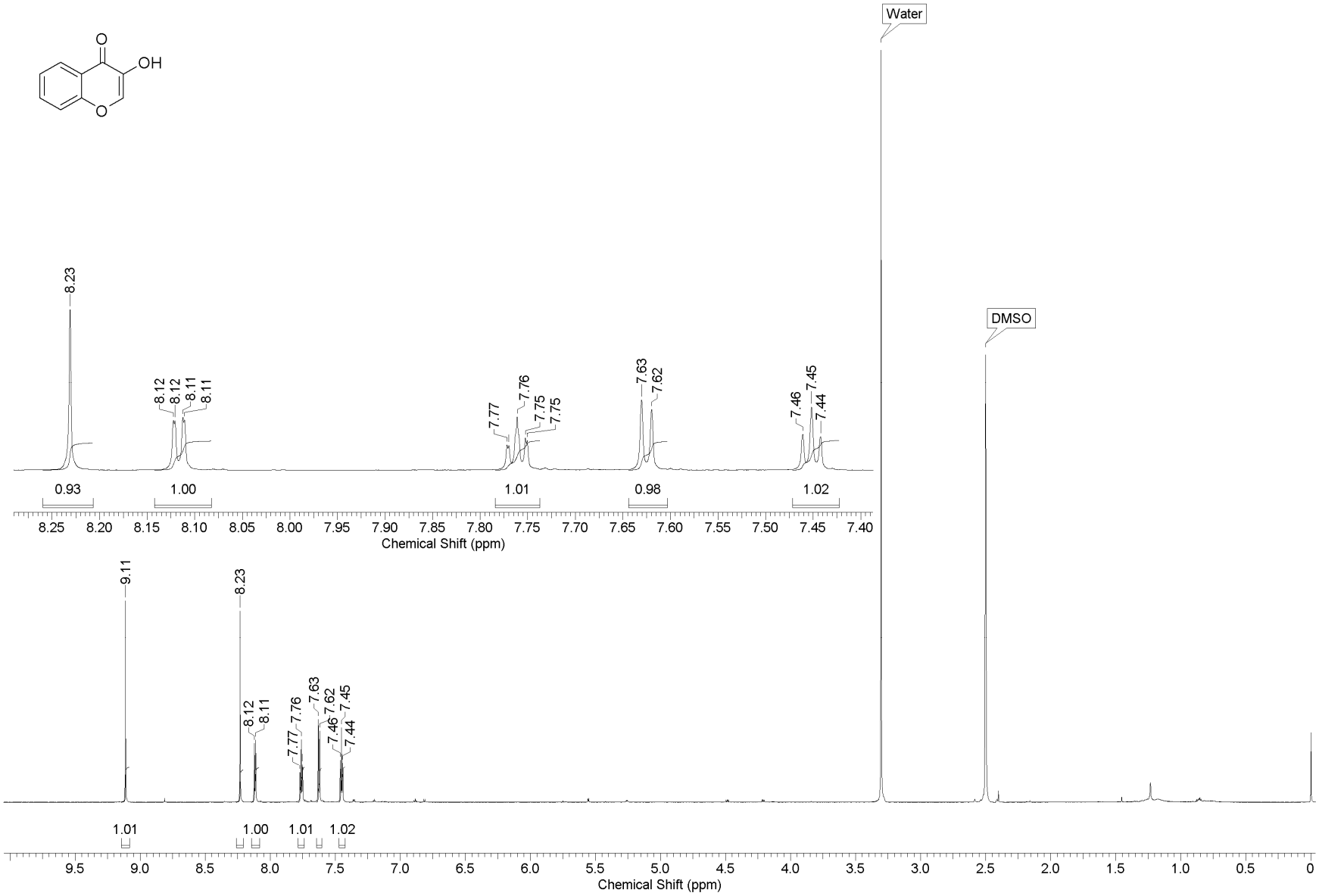

F
O
F
F
O
COOH
DMSO
10.20
10.20
7.67
7.67
7.66
7.66
7.66
7.66
7.65
7.65
7.62
7.62
7.61
7.61
7.53
7.53
7.52
7.52
1.06
1.00
0.99
7.75
7.70
7.65
7.60
7.55
7.50
Chemical Shift (ppm)
0.96
0.99
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

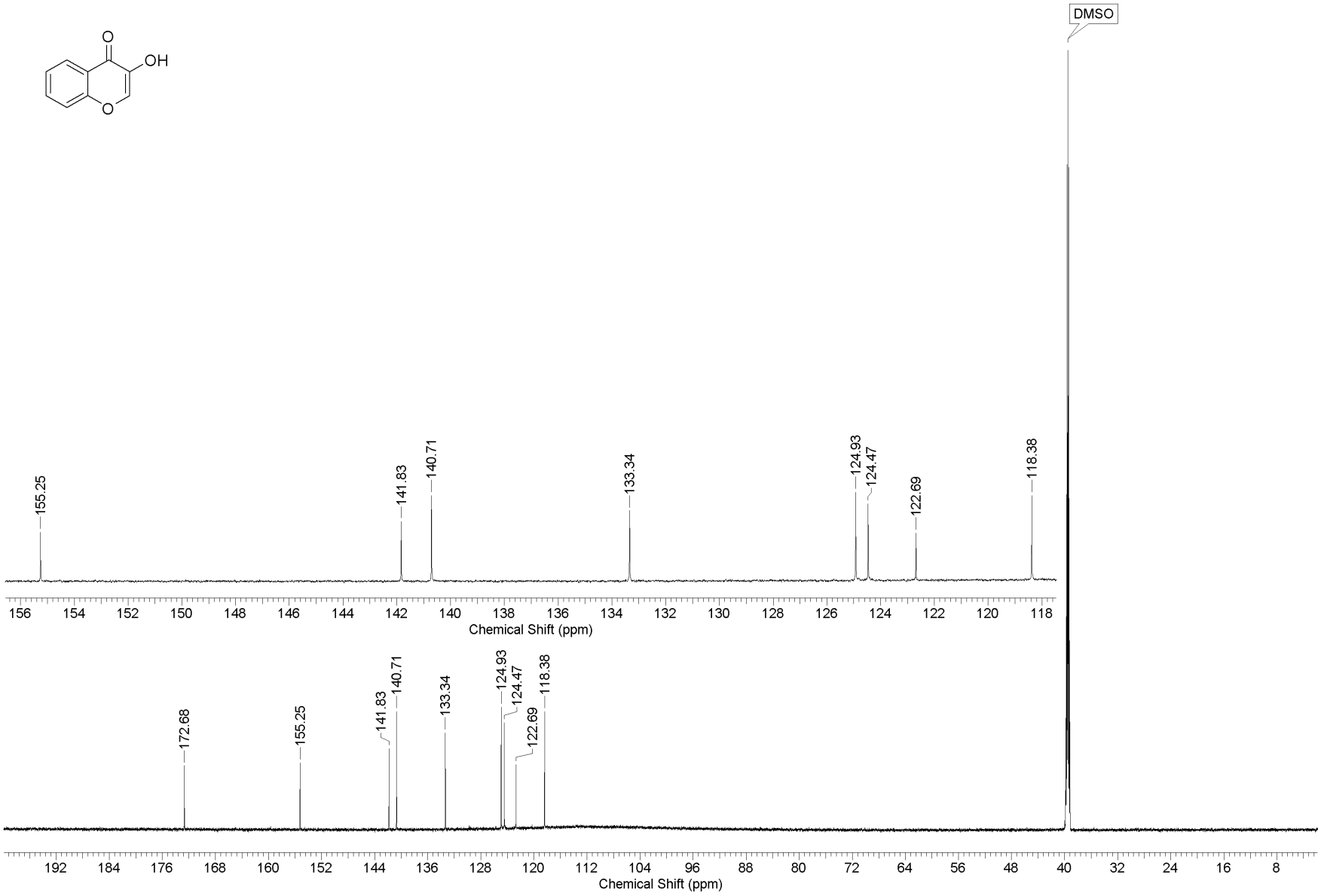

F
O
F
F
O
COOH
DMSO
130.47
130.43
125.33
125.28
122.84
122.72
115.50
114.34
114.22
114.13
112.77
Chemical Shift (ppm)
160.62
160.23
160.04
159.85
159.40
146.71
146.70
Chemical Shift (ppm)
187.48
160.62
159.40
146.70
130.47
130.43
125.33
122.84
122.72
115.50
114.34
114.22
114.13
112.77
Chemical Shift (ppm)

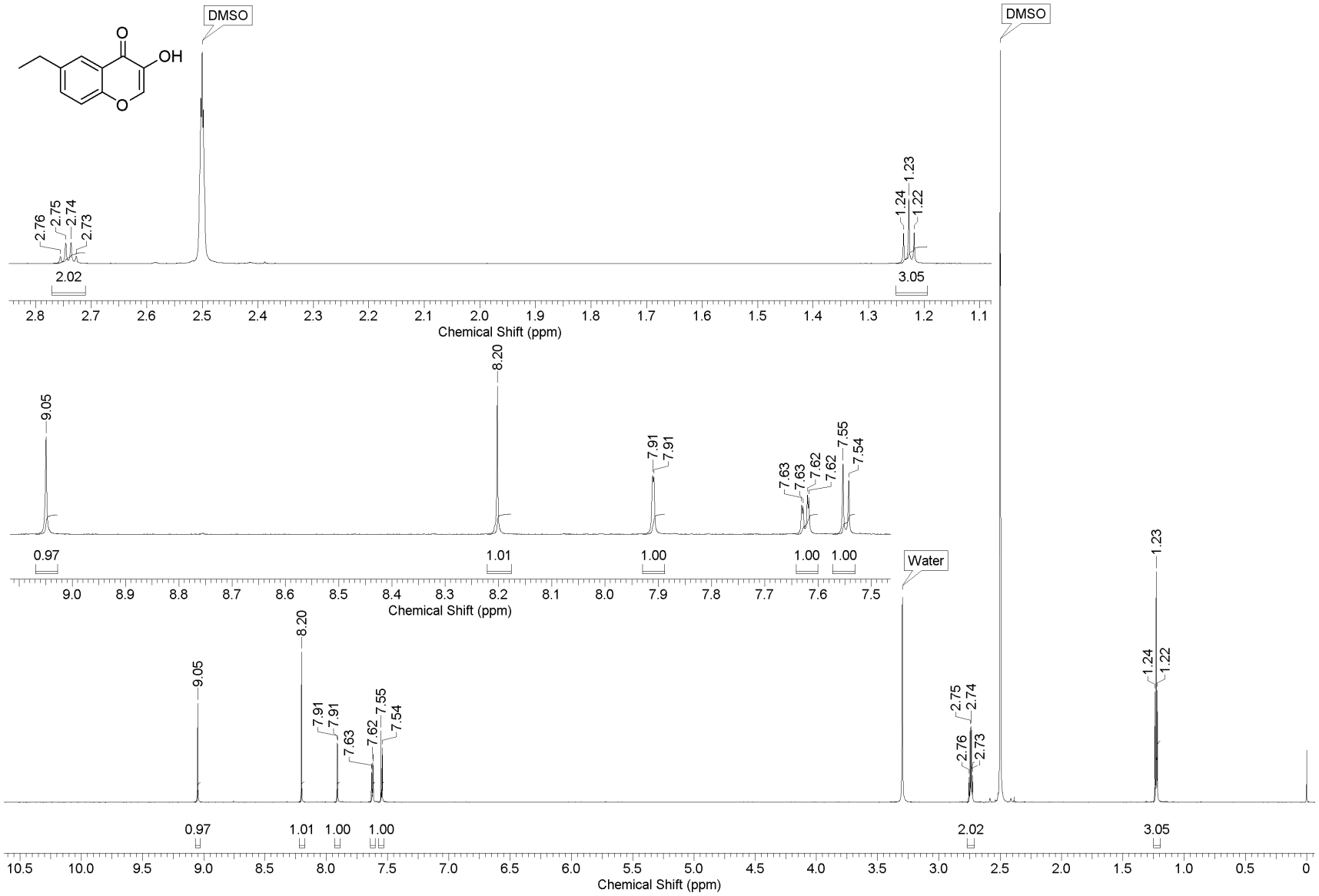

O
F
F
O
COOH
OMe
3.86
DMSO
7.54
7.54
7.53
7.53
7.48
7.47
7.46
7.40
7.40
7.40
7.39
1.00
1.01
1.00
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
Chemical Shift (ppm)
10.21
7.54
7.53
7.53
7.47
7.40
7.40
0.99
1.00
3.09
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

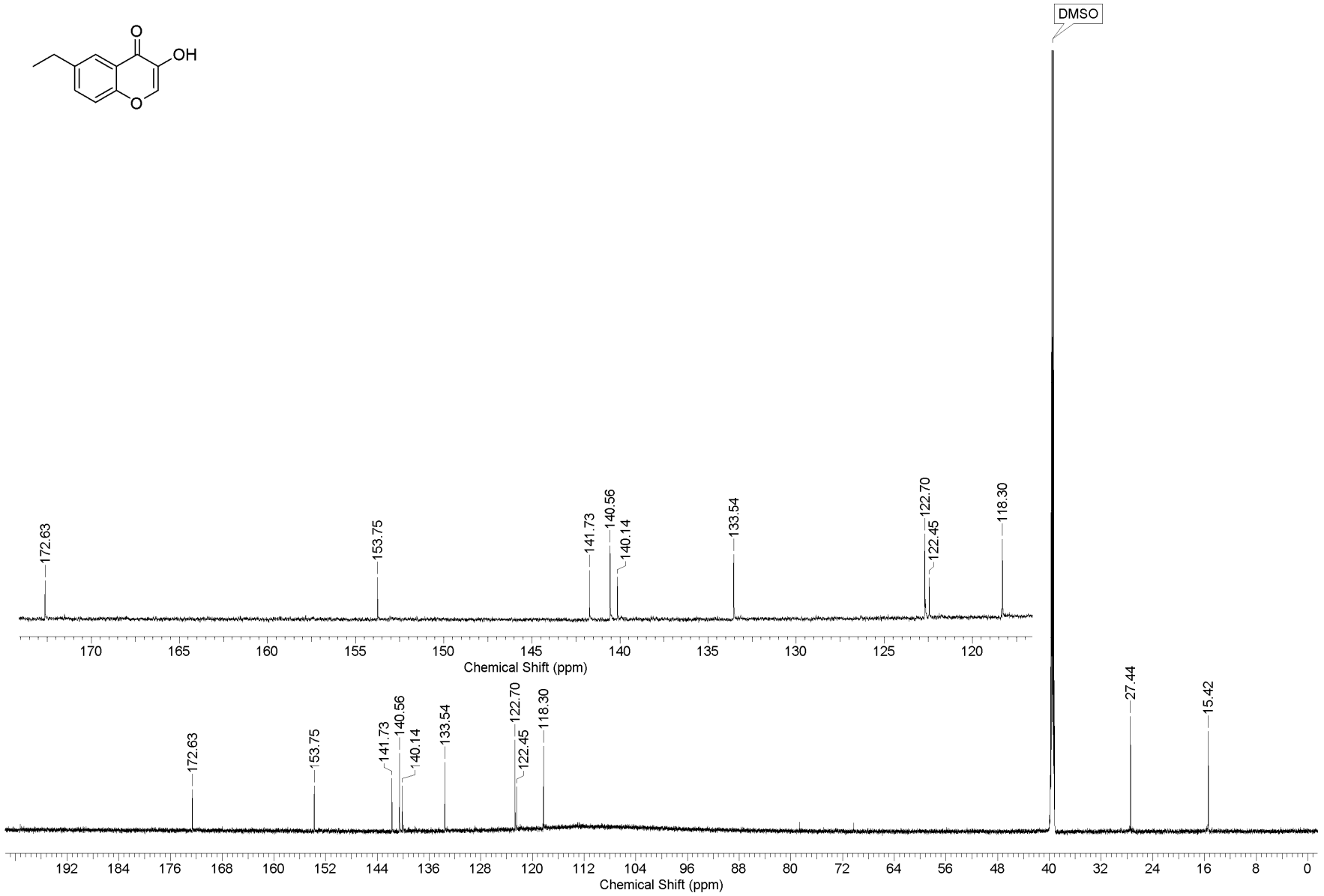

O
F
F
O
COOH
OMe
DMSO
160.46
160.27
160.07
152.79
139.45
130.86
128.11
119.26
118.77
115.56
114.19
112.82
Chemical Shift (ppm)
188.70
56.45

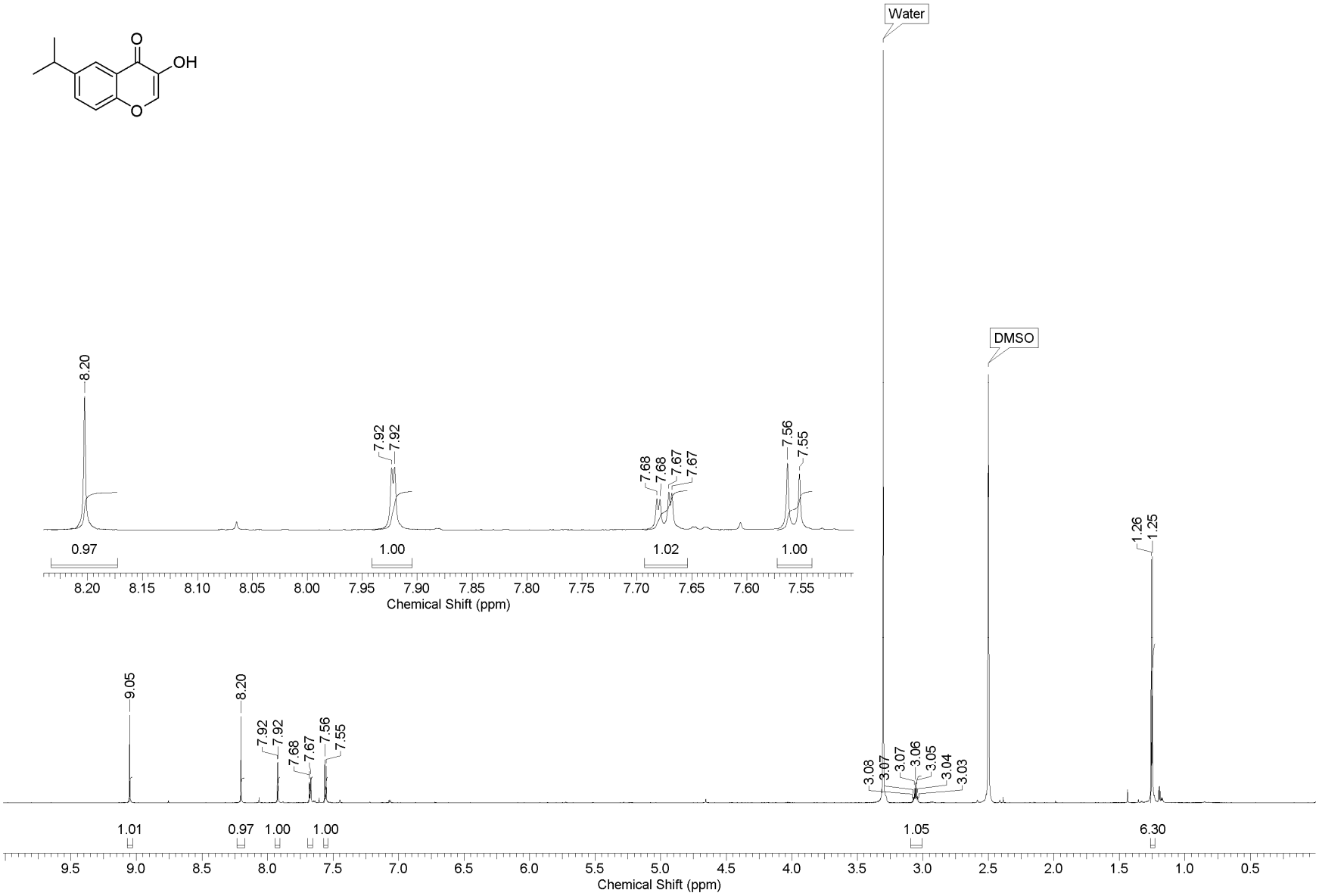

DMSO
2.20
5.01
Water
10.46
7.72
7.72
7.71
7.71
7.62
7.61
7.60
7.60
7.10
7.09
7.09
0.96
1.00
1.96
0.88
1.00
1.96
1.98
3.03
Chemical Shift (ppm)
Chemical Shift (ppm)

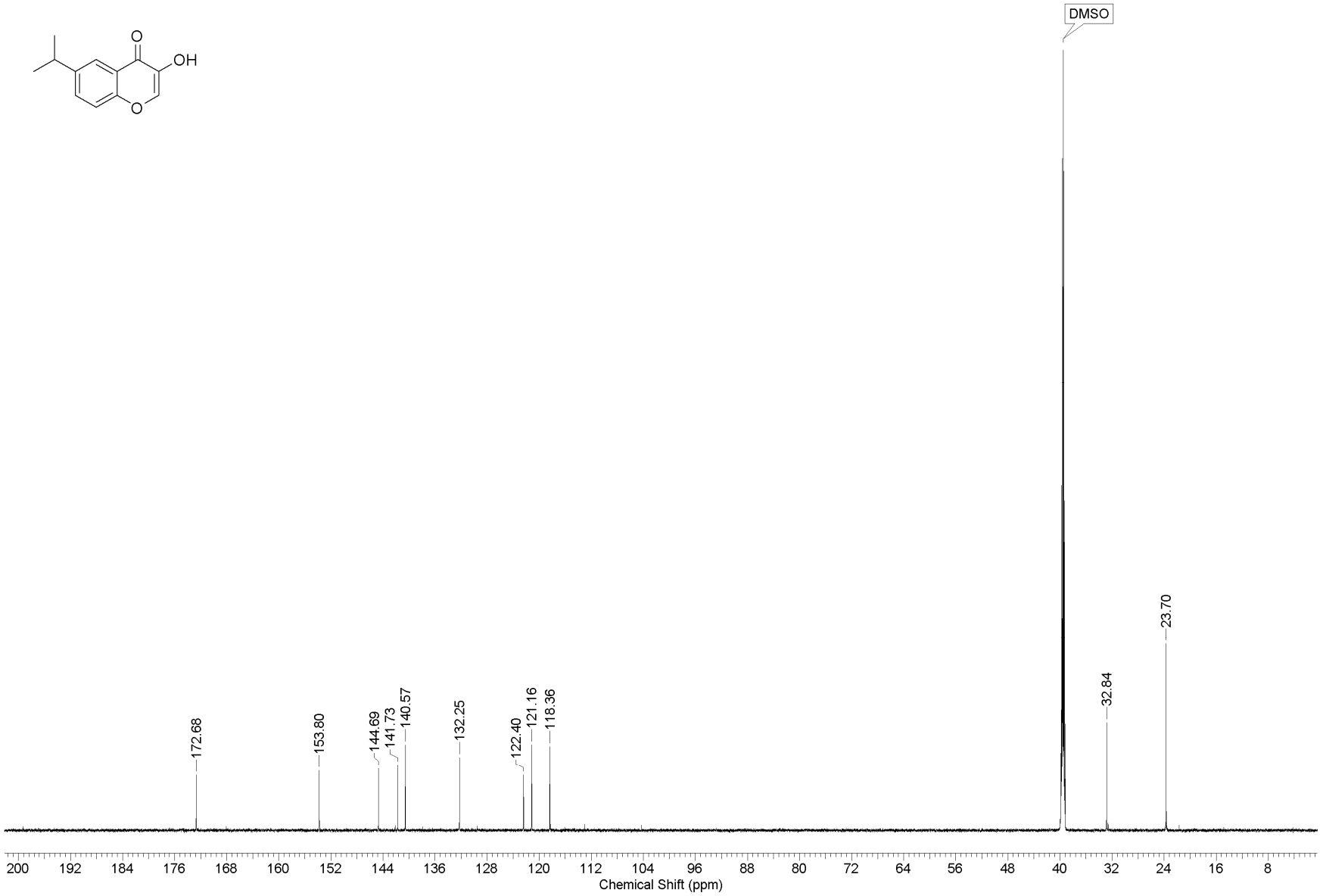

O
OH
O
Water
DMSO
8.23
8.12
8.12
8.11
8.11
7.77
7.76
7.75
7.75
7.63
7.62
7.46
7.45
7.44
0.93
1.00
1.01
0.98
1.02
8.25 8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40
Chemical Shift (ppm)
9.11
8.23
8.12
8.11
7.77
7.76
7.63
7.62
7.46
7.45
7.44
1.01
1.00
1.01
1.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

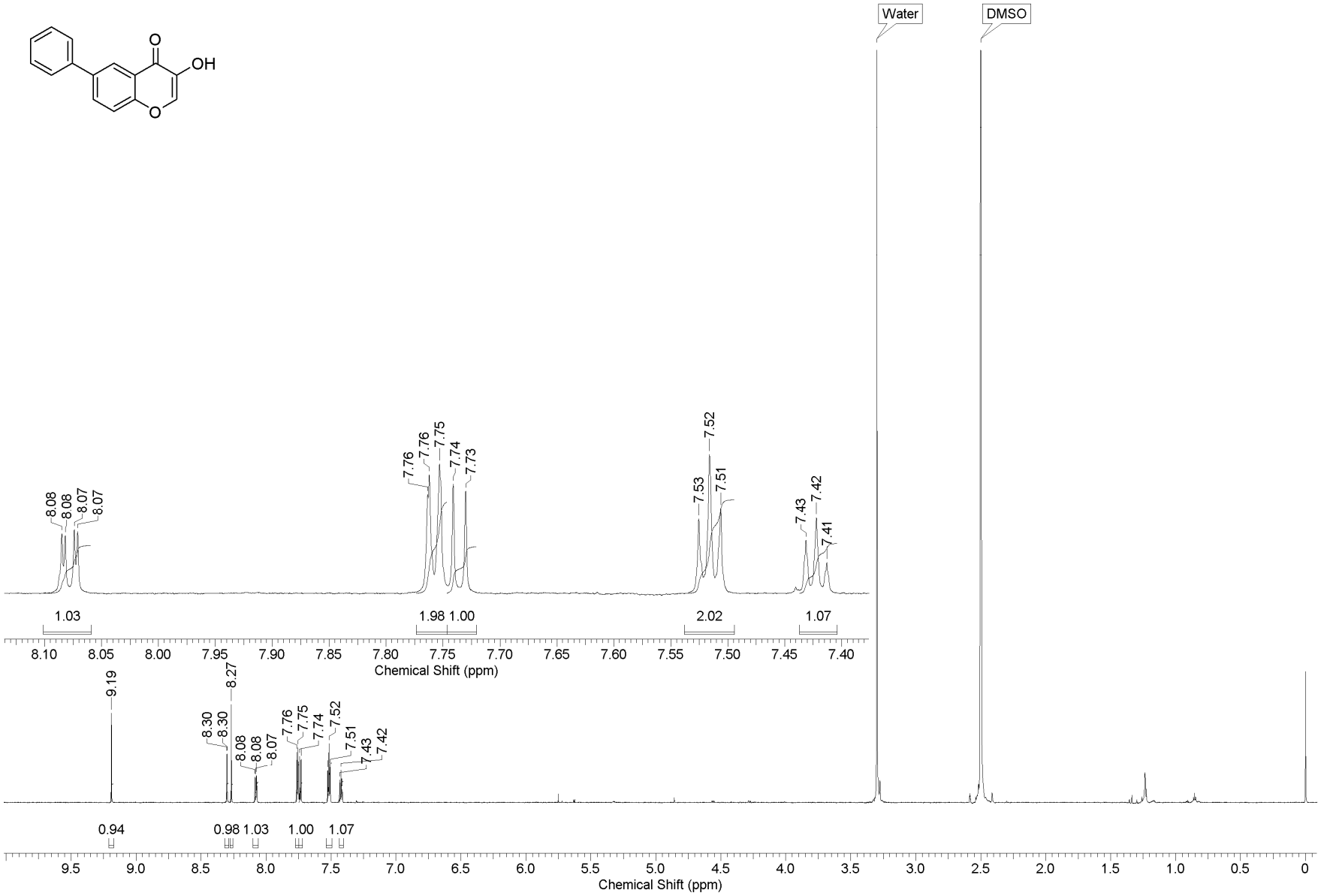

O
OH
O
DMSO
155.25
141.83
140.71
133.34
124.93
124.47
122.69
118.38
156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118
Chemical Shift (ppm)
172.68
155.25
141.83
140.71
133.34
124.93
124.47
122.69
118.38
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)

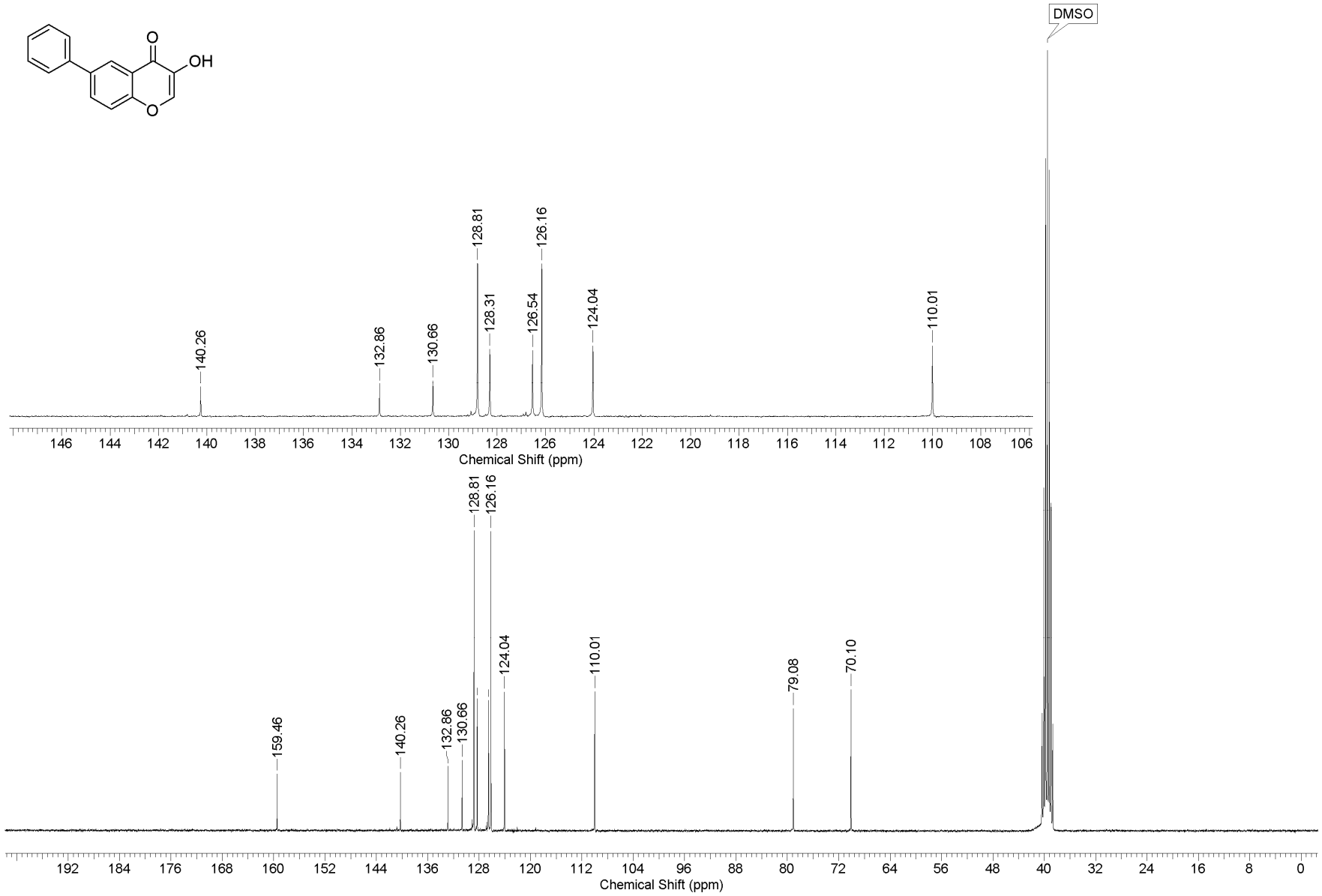

O
OH
O
DMSO
DMSO
2.76
2.75
2.74
2.73
1.24
1.23
1.22
2.02
3.05
Chemical Shift (ppm)
9.05
8.20
7.91
7.91
7.63
7.63
7.62
7.62
7.55
7.54
0.97
1.01
1.00
1.00
1.00
Water
Chemical Shift (ppm)
9.05
8.20
7.91
7.91
7.63
7.62
7.55
7.54
2.76
2.75
2.74
2.73
1.24
1.23
1.22
0.97
1.01
1.00
1.00
2.02
3.05
Chemical Shift (ppm)

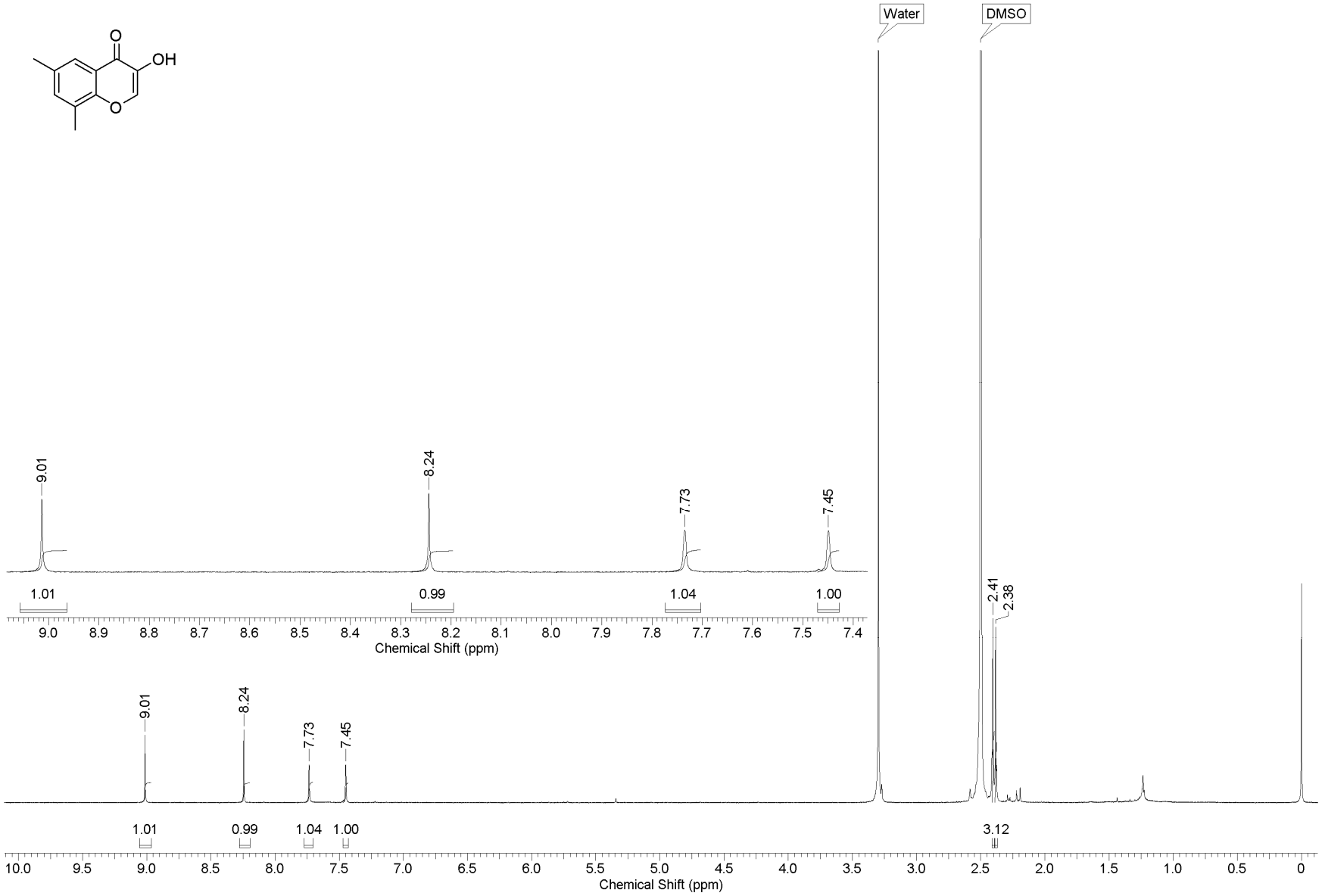

O
OH
O
DMSO
172.63
153.75
141.73
140.56
140.14
133.54
122.70
122.45
118.30
27.44
15.42
Chemical Shift (ppm)
Chemical Shift (ppm)

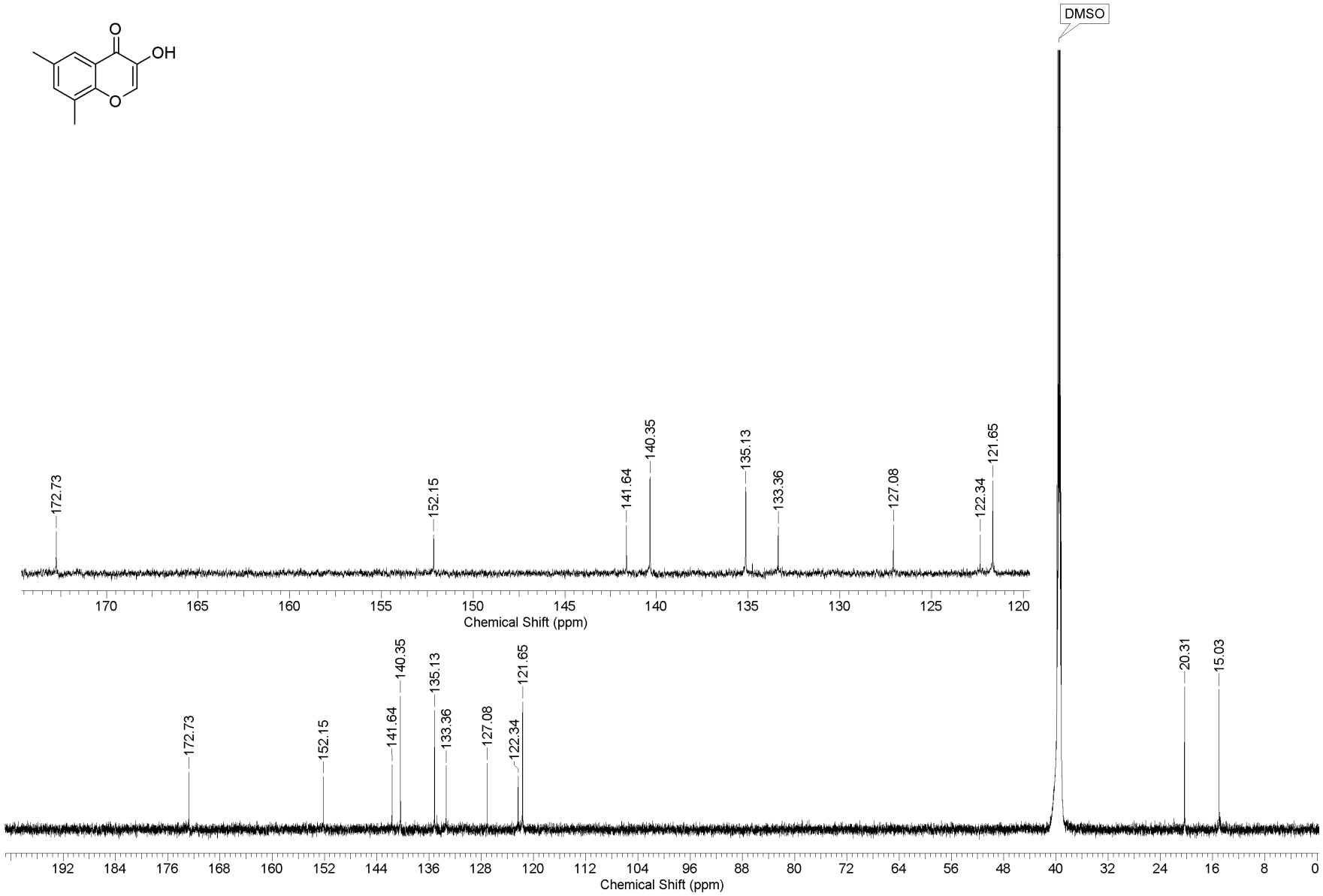

O
OH
O
Water
DMSO
8.20
7.92
7.92
7.68
7.68
7.67
7.67
7.56
7.55
0.97
1.00
1.02
1.00
8.20
8.15
8.10
8.05
8.00
7.95
7.90
7.85
7.80
7.75
7.70
7.65
7.60
7.55
Chemical Shift (ppm)
9.05
8.20
7.92
7.92
7.68
7.67
7.56
7.55
3.08
3.07
3.07
3.06
3.05
3.04
3.03
1.26
1.25
1.01
0.97
1.00
1.00
1.05
6.30
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

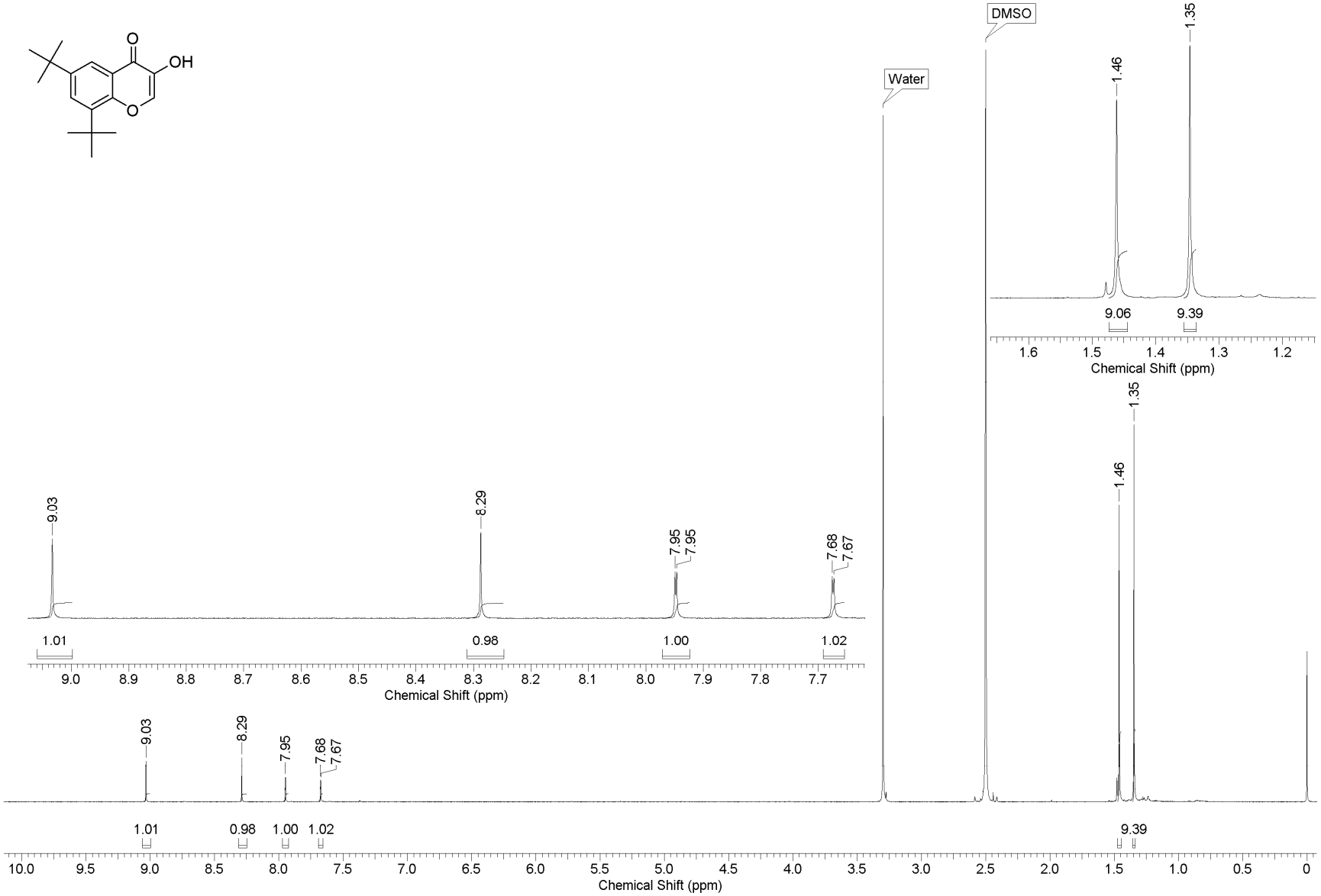

O
OH
O
DMSO
172.68
153.80
144.69
141.73
140.57
132.25
122.40
121.16
118.36
32.84
23.70
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

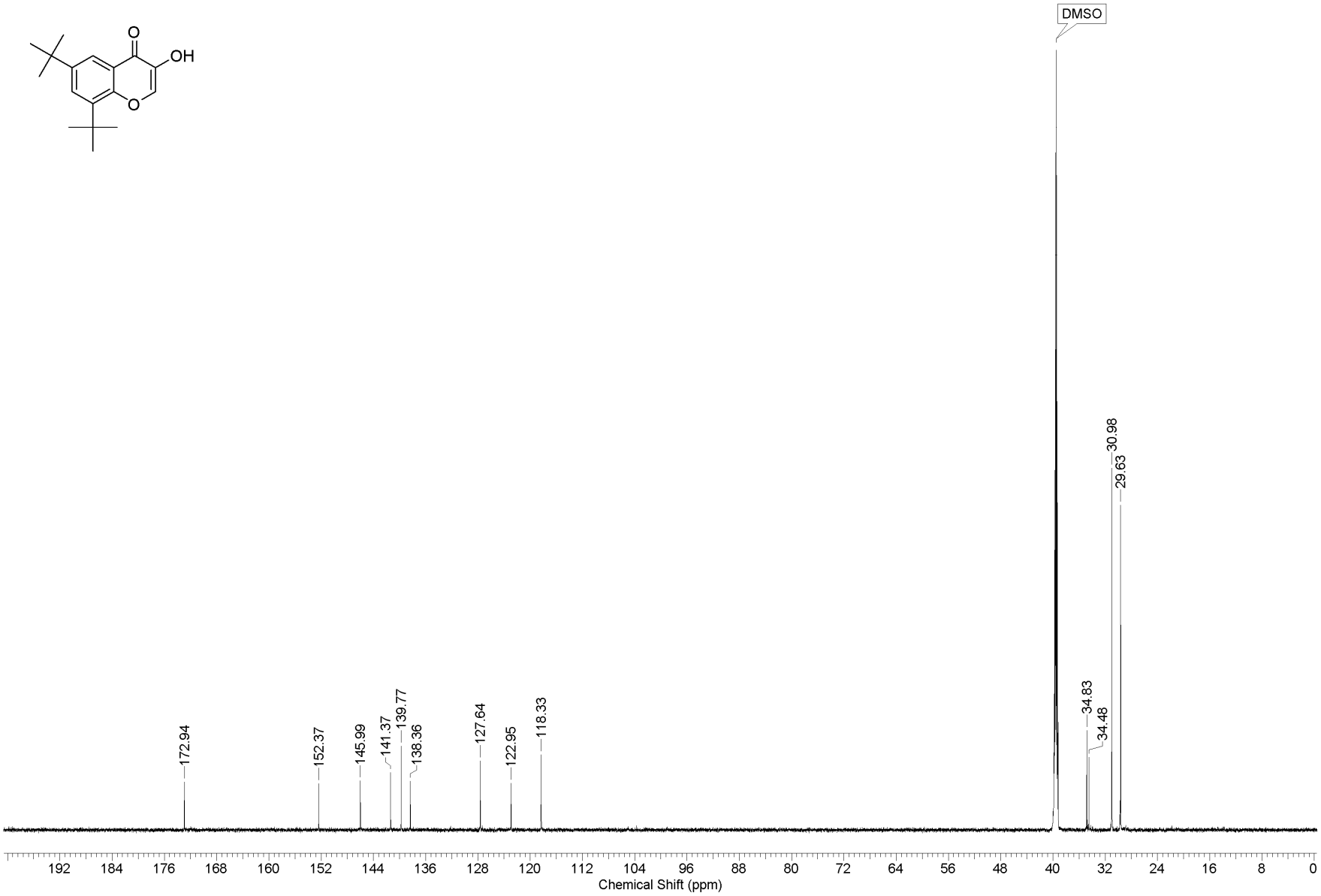

O
OH
O
Water
DMSO
8.08
8.08
8.07
8.07
7.76
7.76
7.75
7.74
7.73
7.53
7.52
7.51
7.43
7.42
7.41
1.03
1.98
1.00
2.02
1.07
Chemical Shift (ppm)
9.19
8.30
8.30
8.27
8.08
8.08
8.07
7.76
7.75
7.74
7.52
7.51
7.43
7.42
0.94
0.98
1.03
1.00
1.07
Chemical Shift (ppm)

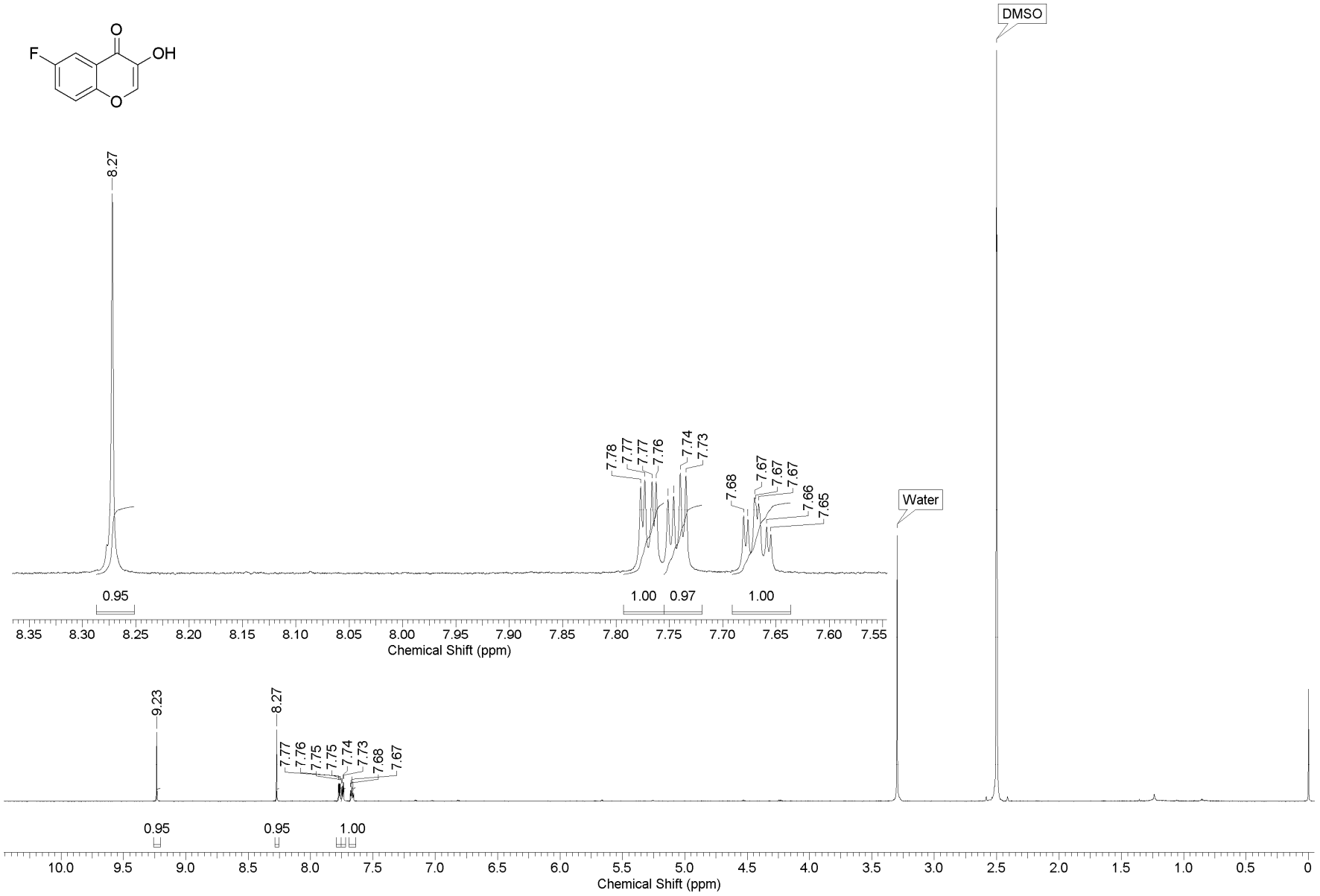

O
OH
O
DMSO
140.26
132.86
130.66
128.81
128.31
126.54
126.16
124.04
110.01
146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106
Chemical Shift (ppm)
159.46
140.26
132.86
130.66
128.81
126.16
124.04
110.01
79.08
70.10
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

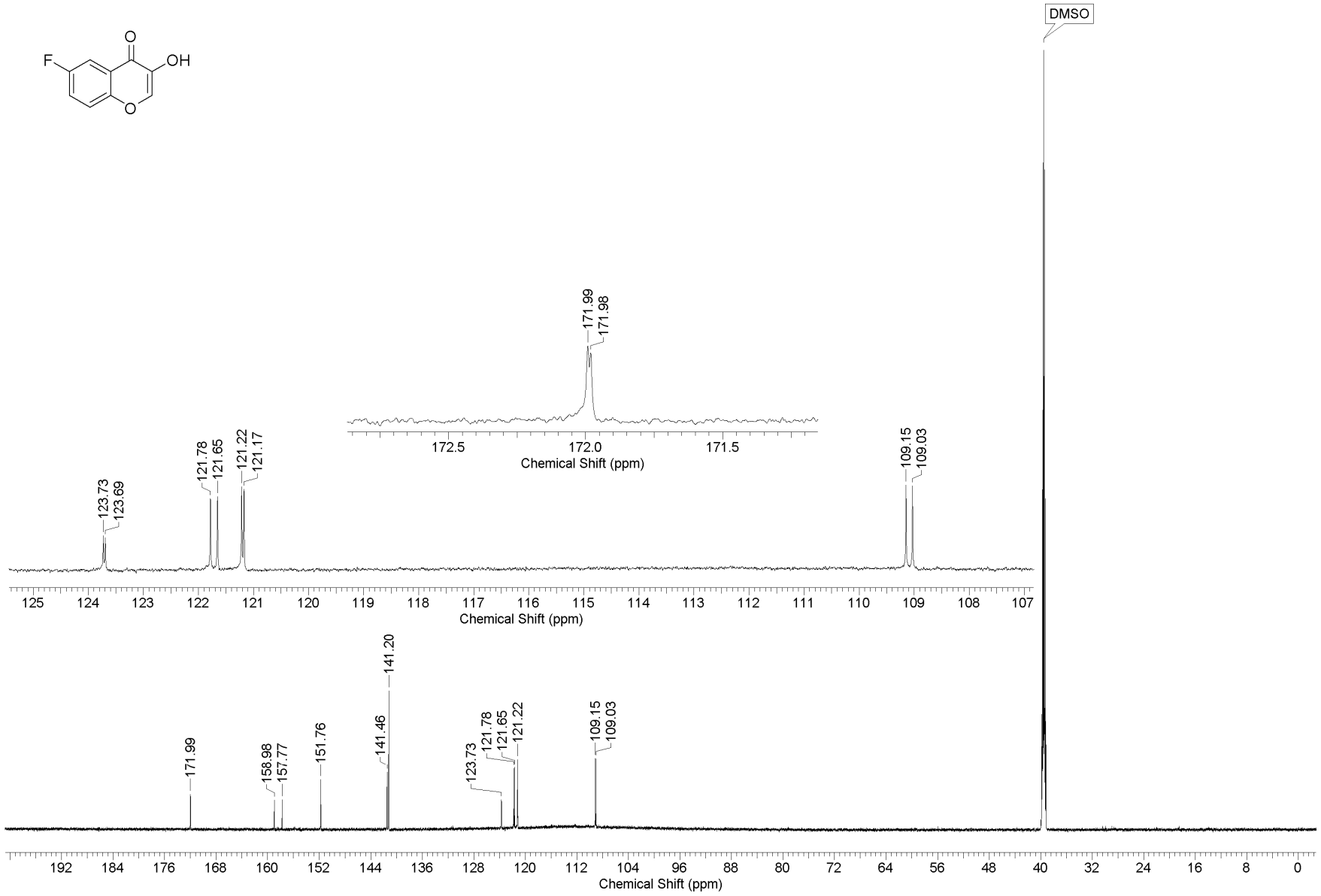

O
OH
O
Water
DMSO
9.01
8.24
7.73
7.45
2.41
2.38
1.01
0.99
1.04
1.00
3.12
Chemical Shift (ppm)

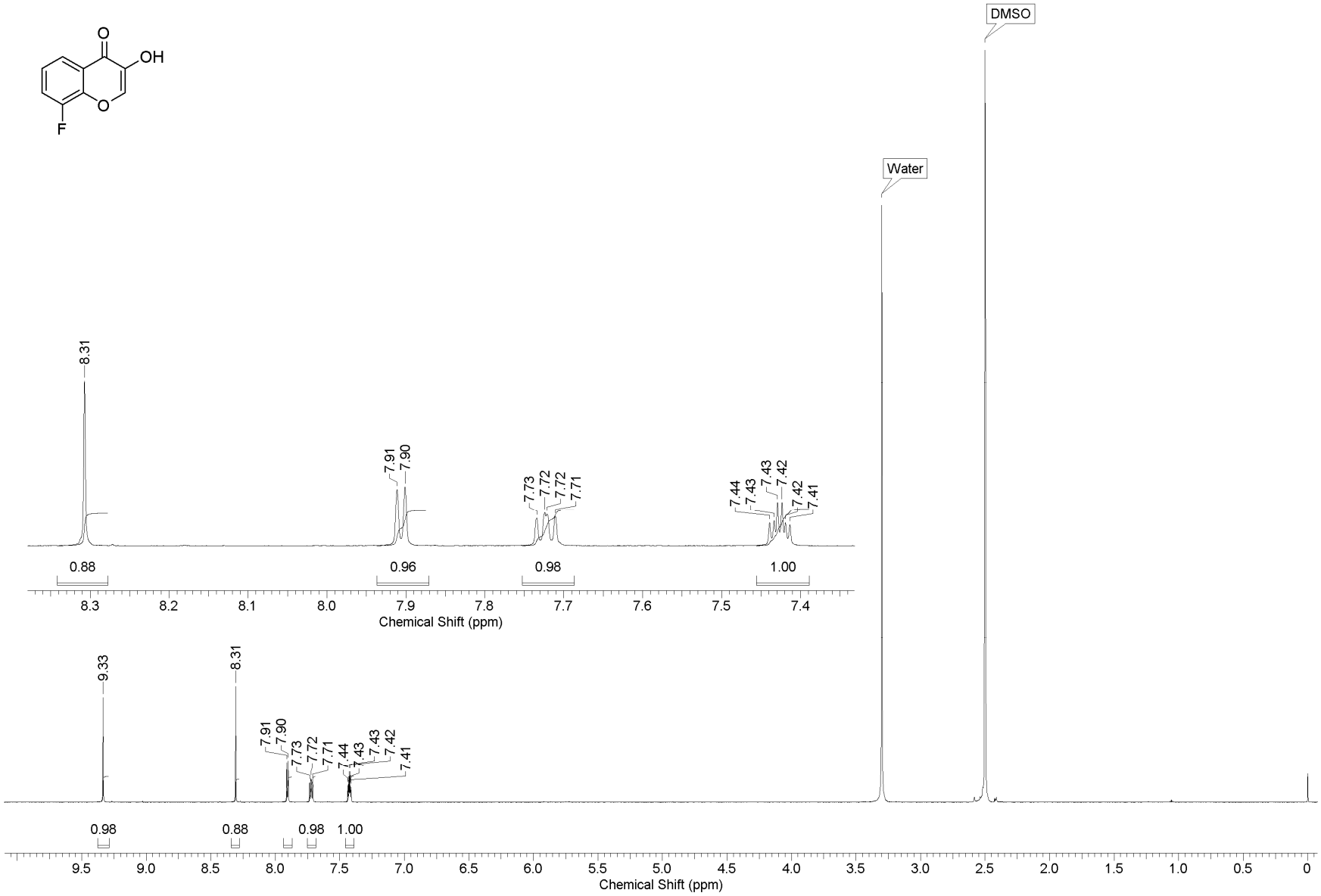

O
OH
O
DMSO
172.73
152.15
141.64
140.35
135.13
133.36
127.08
122.34
121.65
20.31
15.03
Chemical Shift (ppm)
Chemical Shift (ppm)

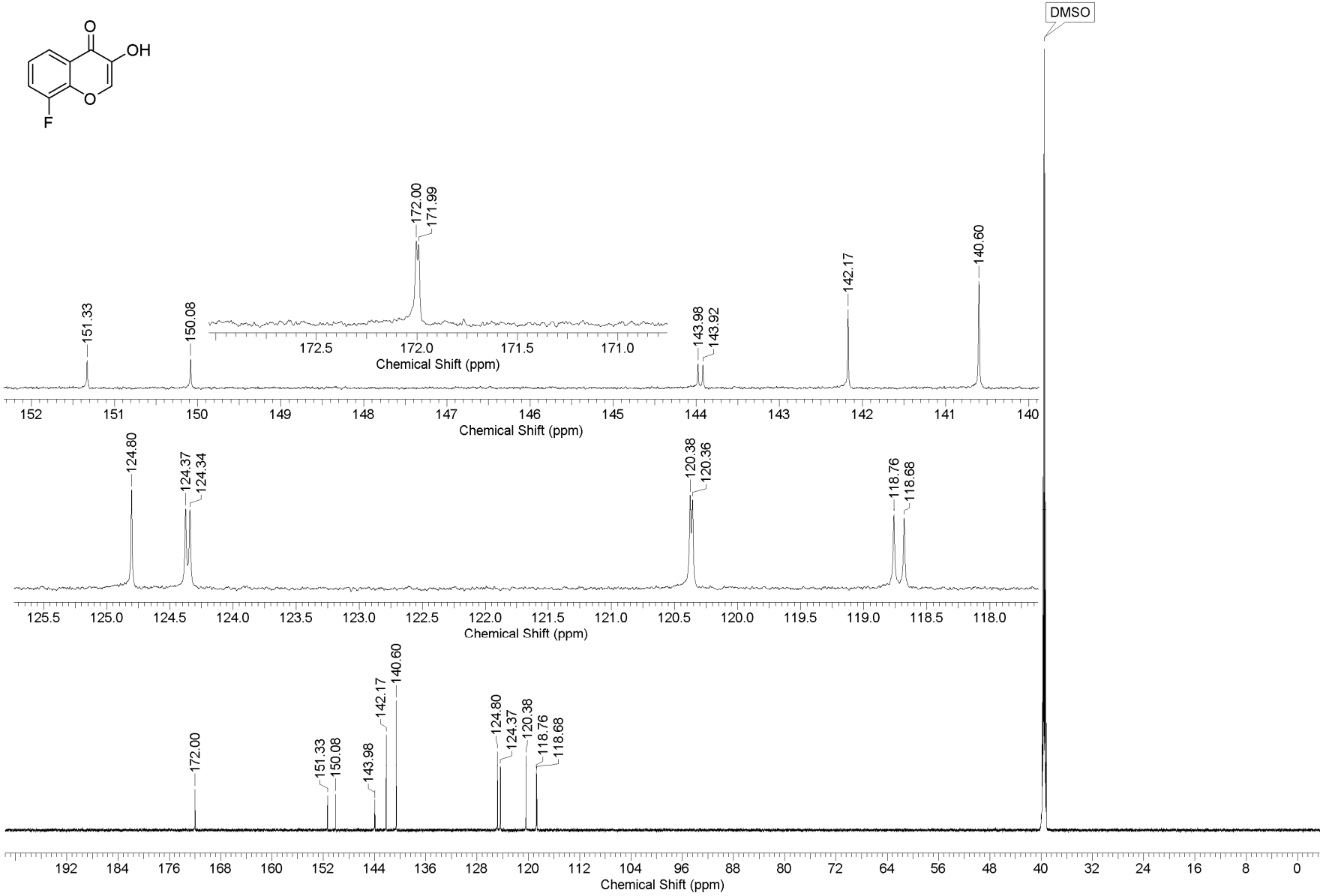

O
OH
O
DMSO
Water
1.35
1.46
9.06
9.39
1.6
1.5
1.4
1.3
1.2
Chemical Shift (ppm)
9.03
8.29
7.95
7.95
7.68
7.67
1.01
0.98
1.00
1.02
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
Chemical Shift (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

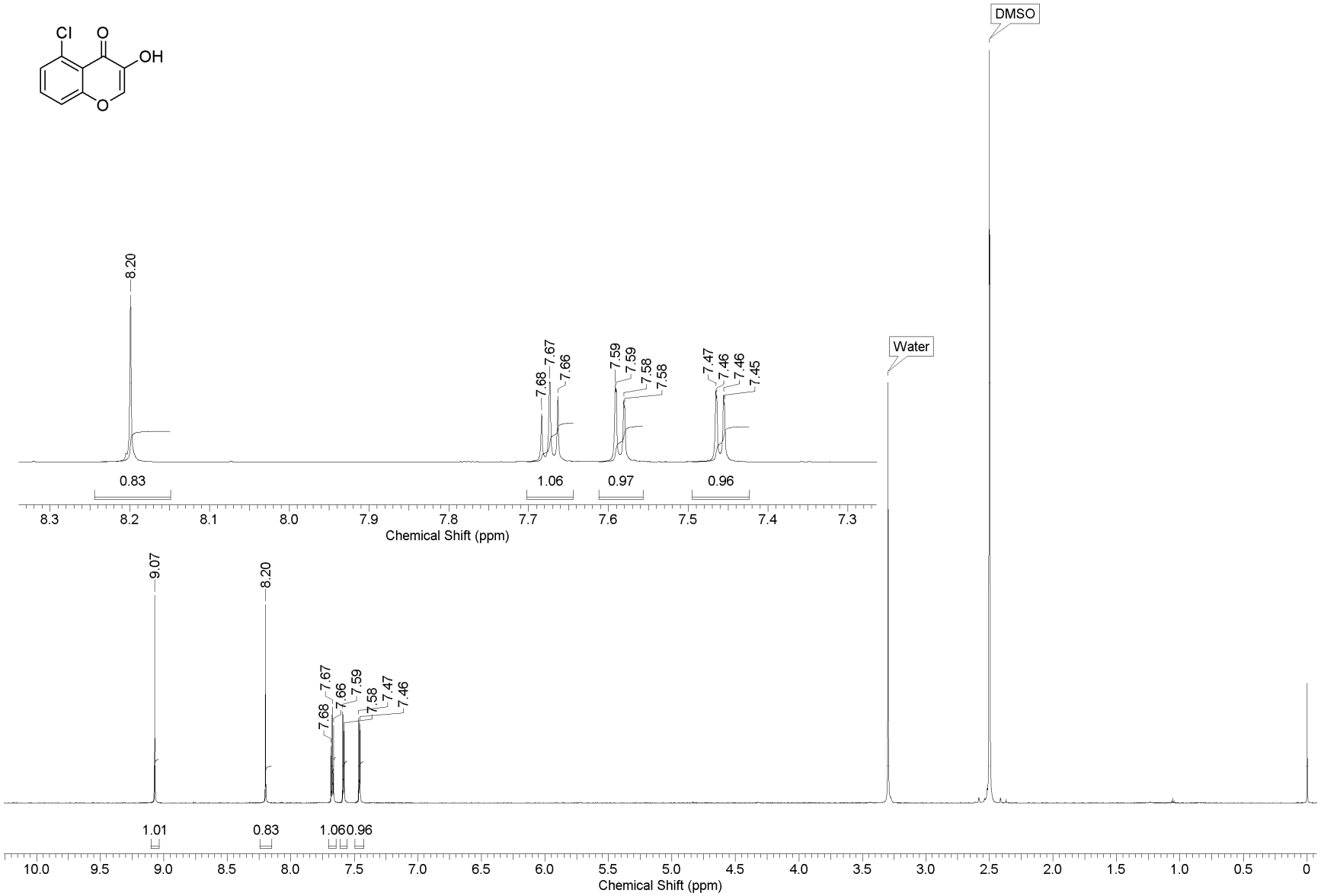

O
OH
O
DMSO
172.94
152.37
145.99
141.37
139.77
138.36
127.64
122.95
118.33
34.83
34.48
30.98
29.63
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

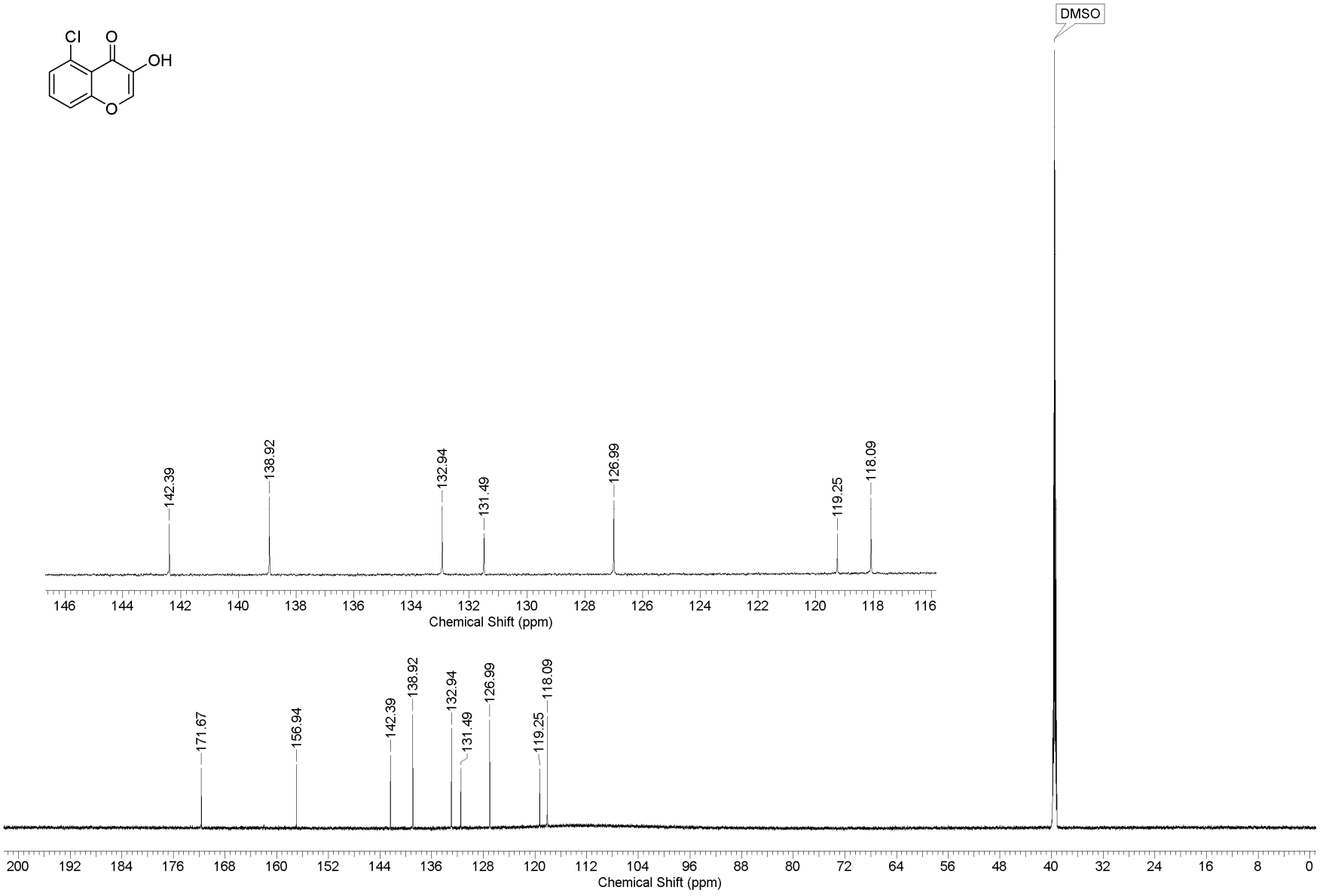

F
O
OH
O
DMSO
Water
8.27
7.78
7.77
7.77
7.76
7.74
7.73
7.68
7.67
7.67
7.67
7.66
7.65
0.95
1.00
0.97
1.00
8.35 8.30 8.25 8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55
Chemical Shift (ppm)
9.23
8.27
7.77
7.76
7.75
7.75
7.74
7.73
7.68
7.67
0.95
0.95
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

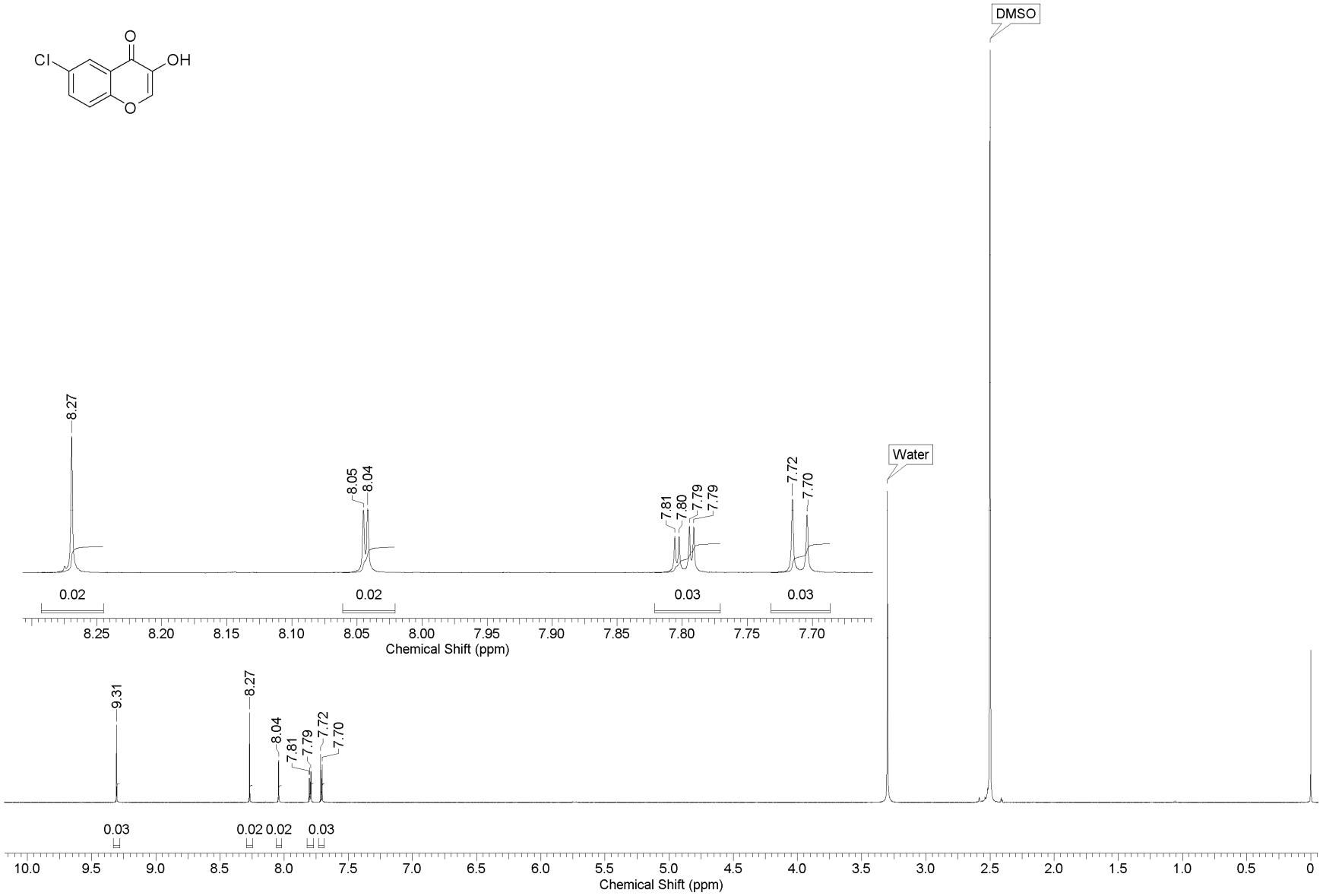

F
O
OH
O
DMSO
171.99
171.98
172.5
172.0
171.5
Chemical Shift (ppm)
123.73
123.69
121.78
121.65
121.22
121.17
109.15
109.03
125
124
123
122
121
120
119
118
117
116
115
114
113
112
111
110
109
108
107
Chemical Shift (ppm)
141.20
171.99
158.98
157.77
151.76
141.46
123.73
121.78
121.65
121.22
109.15
109.03
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

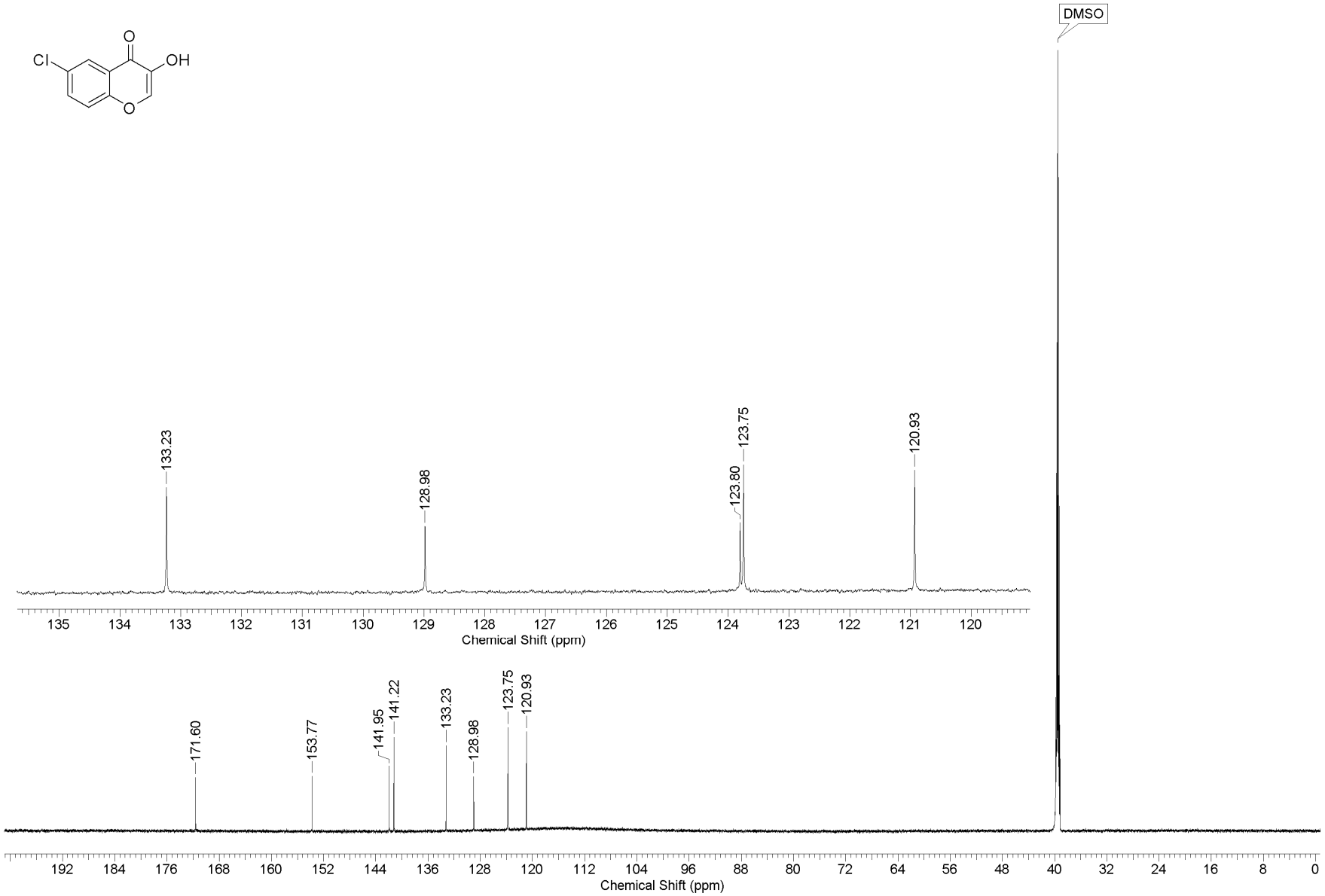

O
OH
O
F
DMSO
Water
8.31
7.91
7.90
7.73
7.72
7.72
7.71
7.44
7.43
7.43
7.42
7.42
7.41
0.88
0.96
0.98
1.00
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
Chemical Shift (ppm)
9.33
8.31
7.91
7.90
7.73
7.72
7.71
7.44
7.43
7.43
7.42
7.41
0.98
0.88
0.98
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

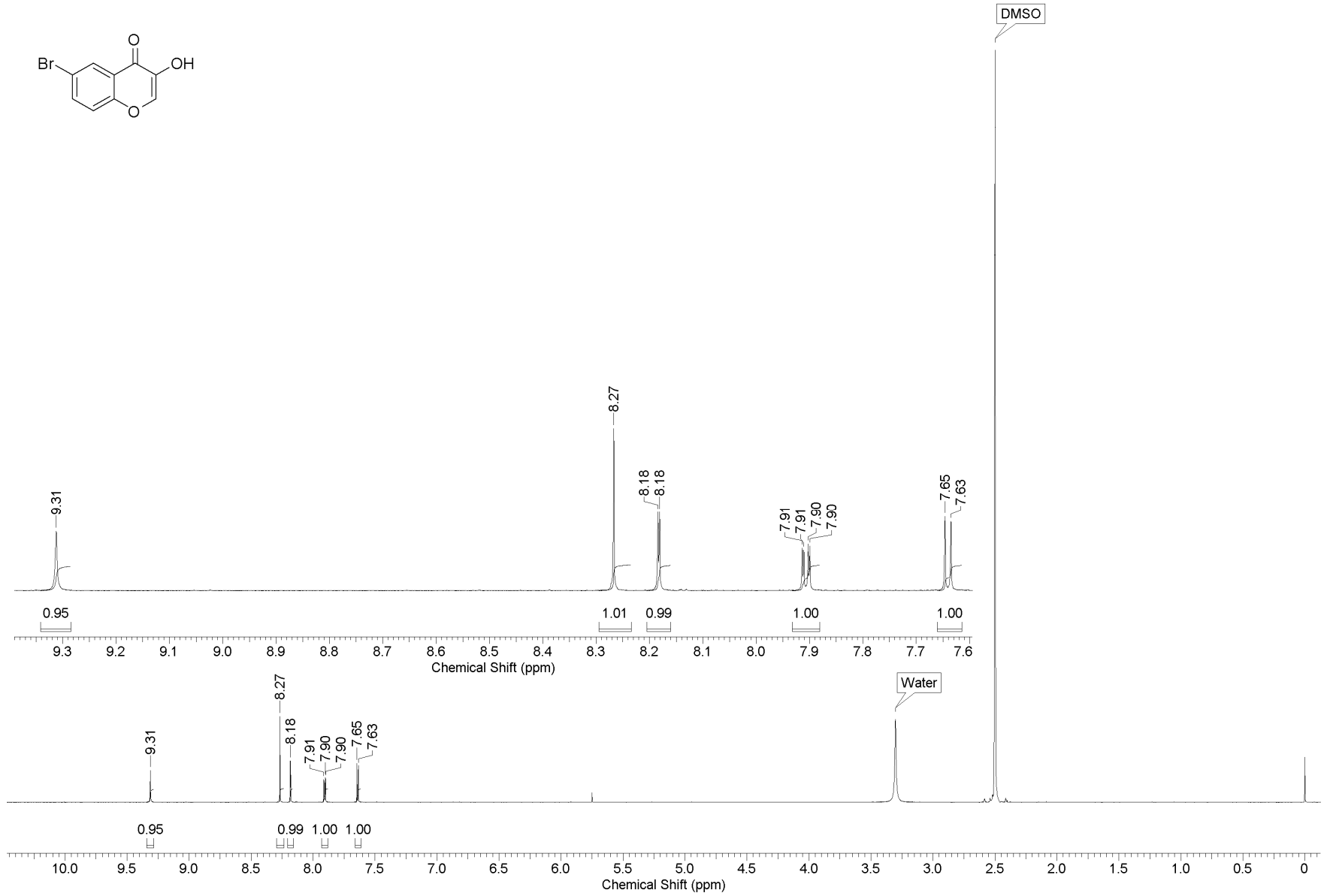

O
OH
O
F
DMSO
172.00
171.99
151.33
150.08
143.98
143.92
142.17
140.60
Chemical Shift (ppm)
124.80
124.37
124.34
120.38
120.36
118.76
118.68
Chemical Shift (ppm)
172.00
151.33
150.08
143.98
142.17
140.60
124.80
124.37
120.38
118.76
118.68
Chemical Shift (ppm)

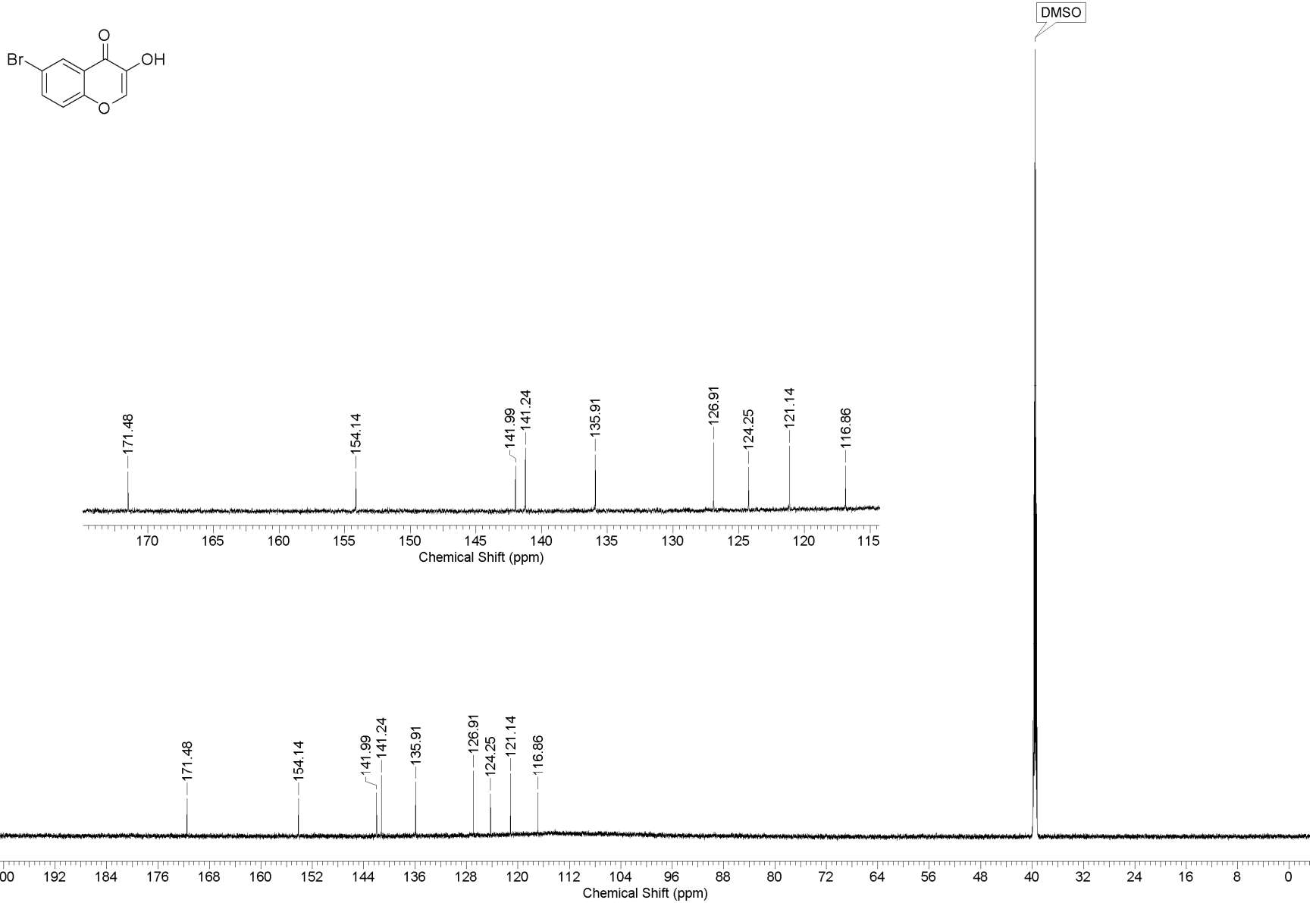

Cl
O
OH
O
DMSO
Water
8.20
7.68
7.67
7.66
7.59
7.59
7.58
7.58
7.47
7.46
7.46
7.45
0.83
1.06
0.97
0.96
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
Chemical Shift (ppm)
9.07
8.20
7.68
7.67
7.66
7.59
7.58
7.47
7.46
1.01
0.83
1.06
0.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

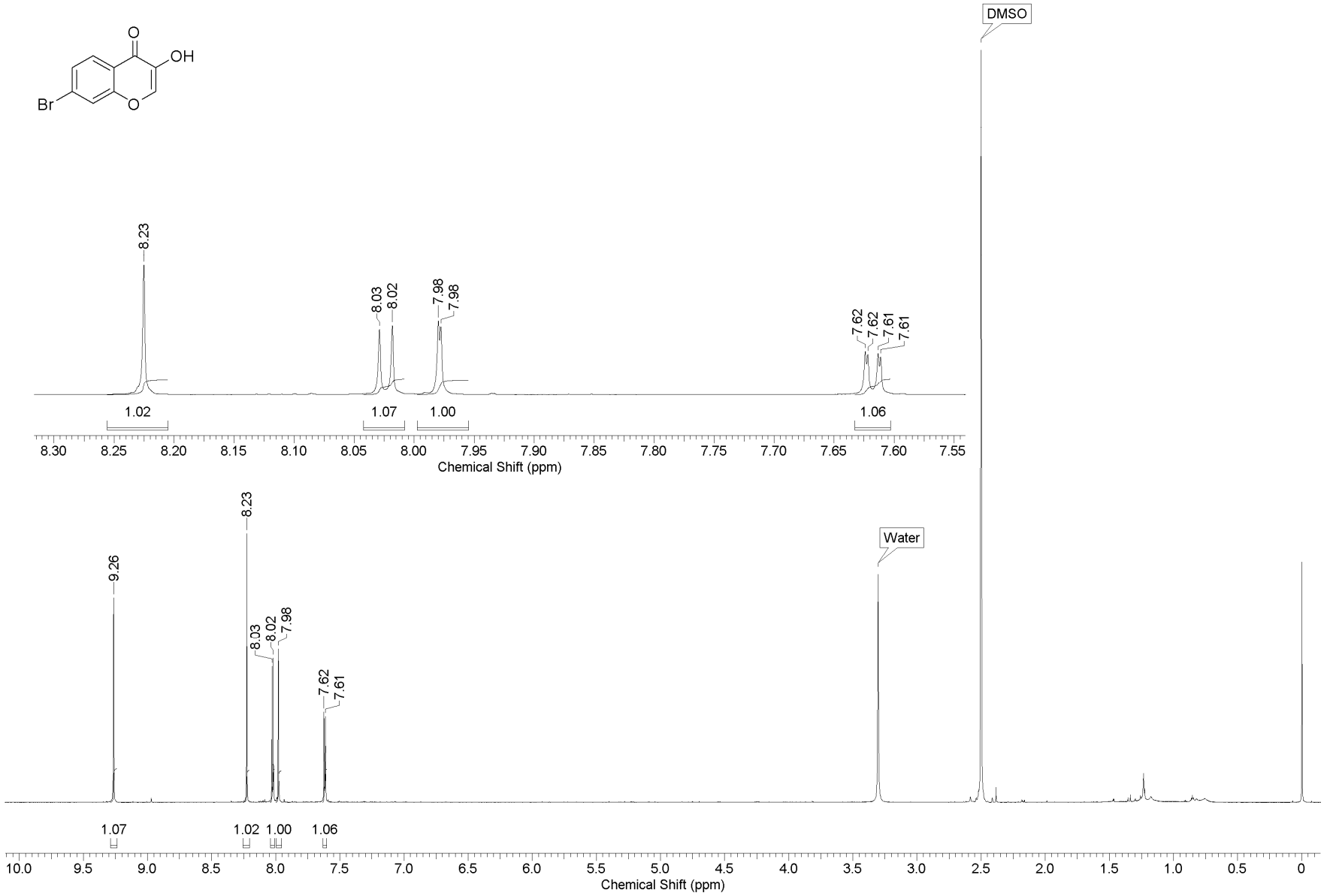

Cl
O
OH
O
DMSO
142.39
138.92
132.94
131.49
126.99
119.25
118.09
146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116
Chemical Shift (ppm)
171.67
156.94
142.39
138.92
132.94
131.49
126.99
119.25
118.09
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

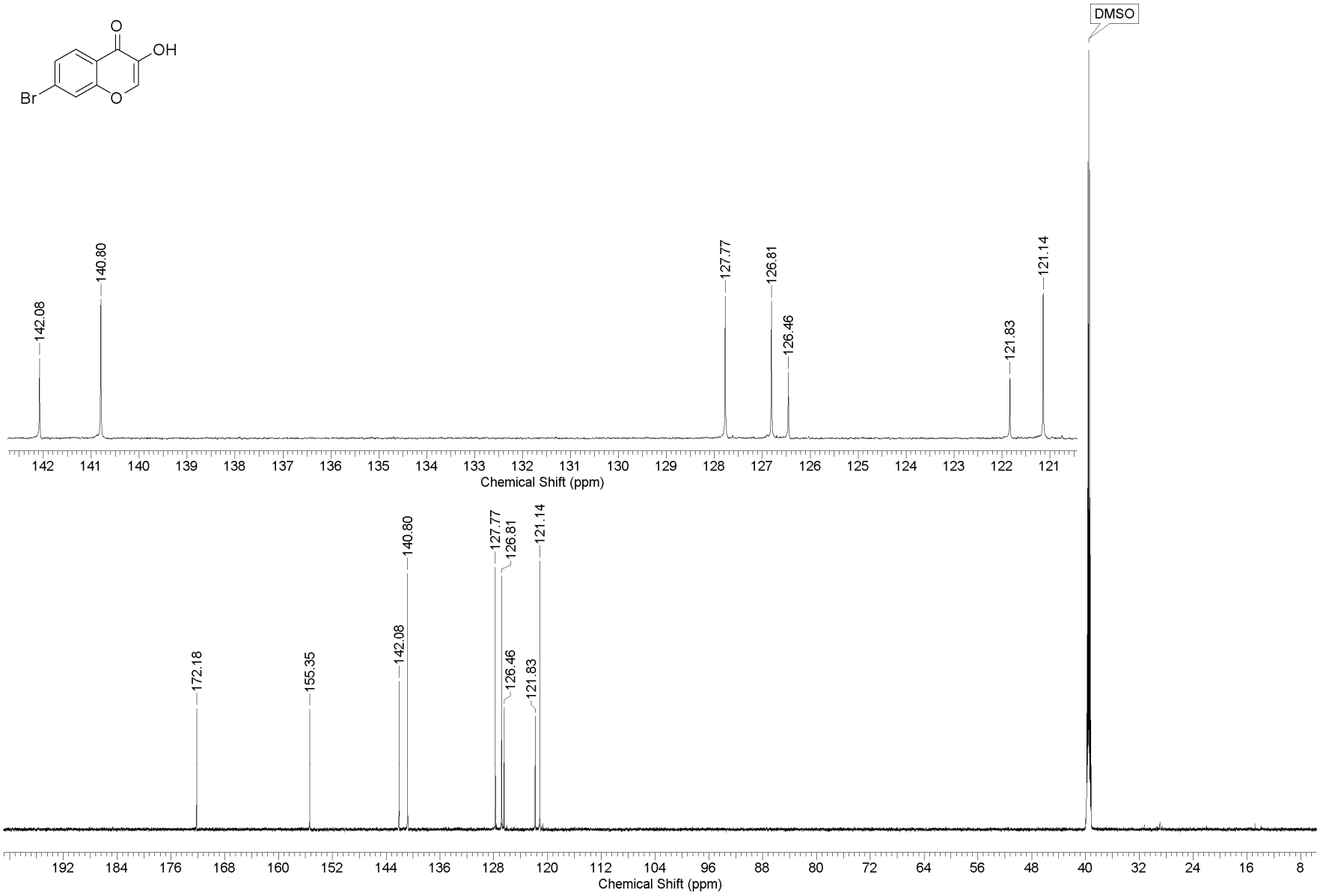

Cl
O
OH
O
DMSO
Water
8.27
8.05
8.04
7.81
7.80
7.79
7.79
7.72
7.70
0.02
0.02
0.03
0.03
8.25
8.20
8.15
8.10
8.05
8.00
7.95
7.90
7.85
7.80
7.75
7.70
Chemical Shift (ppm)
9.31
8.27
8.04
7.81
7.79
7.72
7.70
0.03
0.02
0.02
0.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

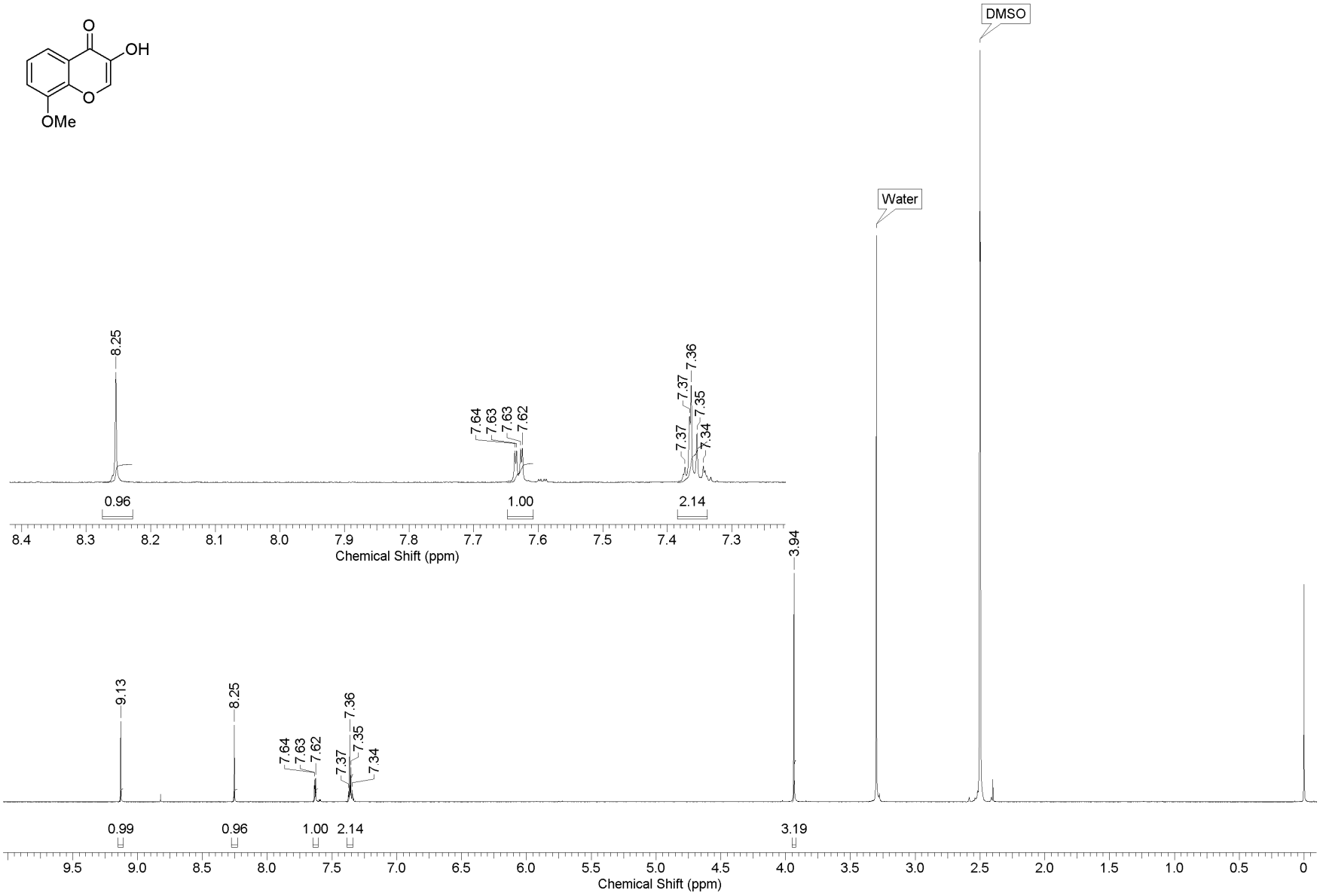

Cl
O
OH
O
DMSO
133.23
128.98
123.80
123.75
120.93
135
134
133
132
131
130
129
128
127
126
125
124
123
122
121
120
Chemical Shift (ppm)
171.60
153.77
141.95
141.22
133.23
128.98
123.75
120.93
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

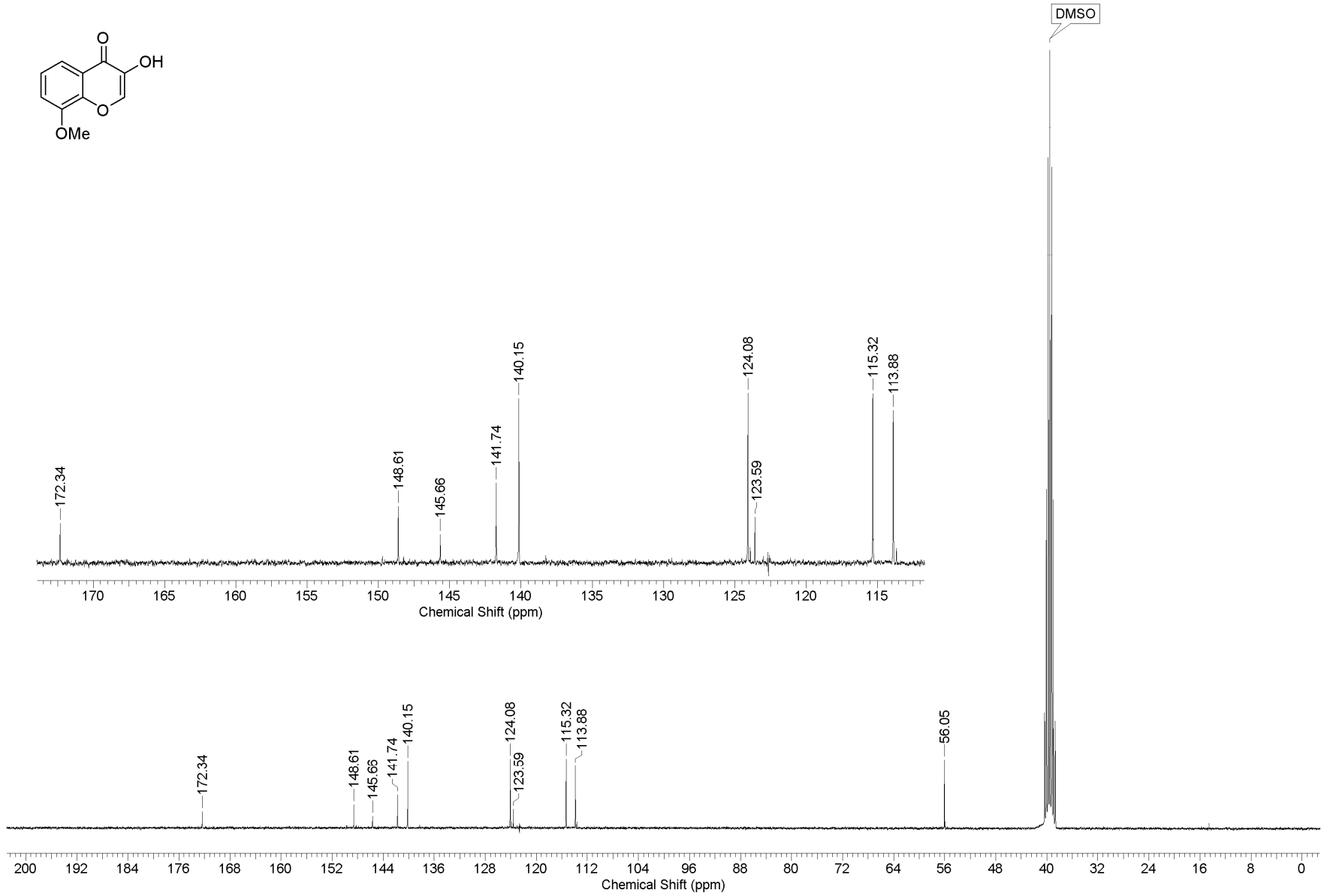

Br
O
OH
O
DMSO
9.31
8.27
8.18
8.18
7.91
7.91
7.90
7.90
7.65
7.63
0.95
1.01
0.99
1.00
1.00
9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6
Chemical Shift (ppm)
Water
9.31
8.27
8.18
7.91
7.90
7.90
7.65
7.63
0.95
0.99
1.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

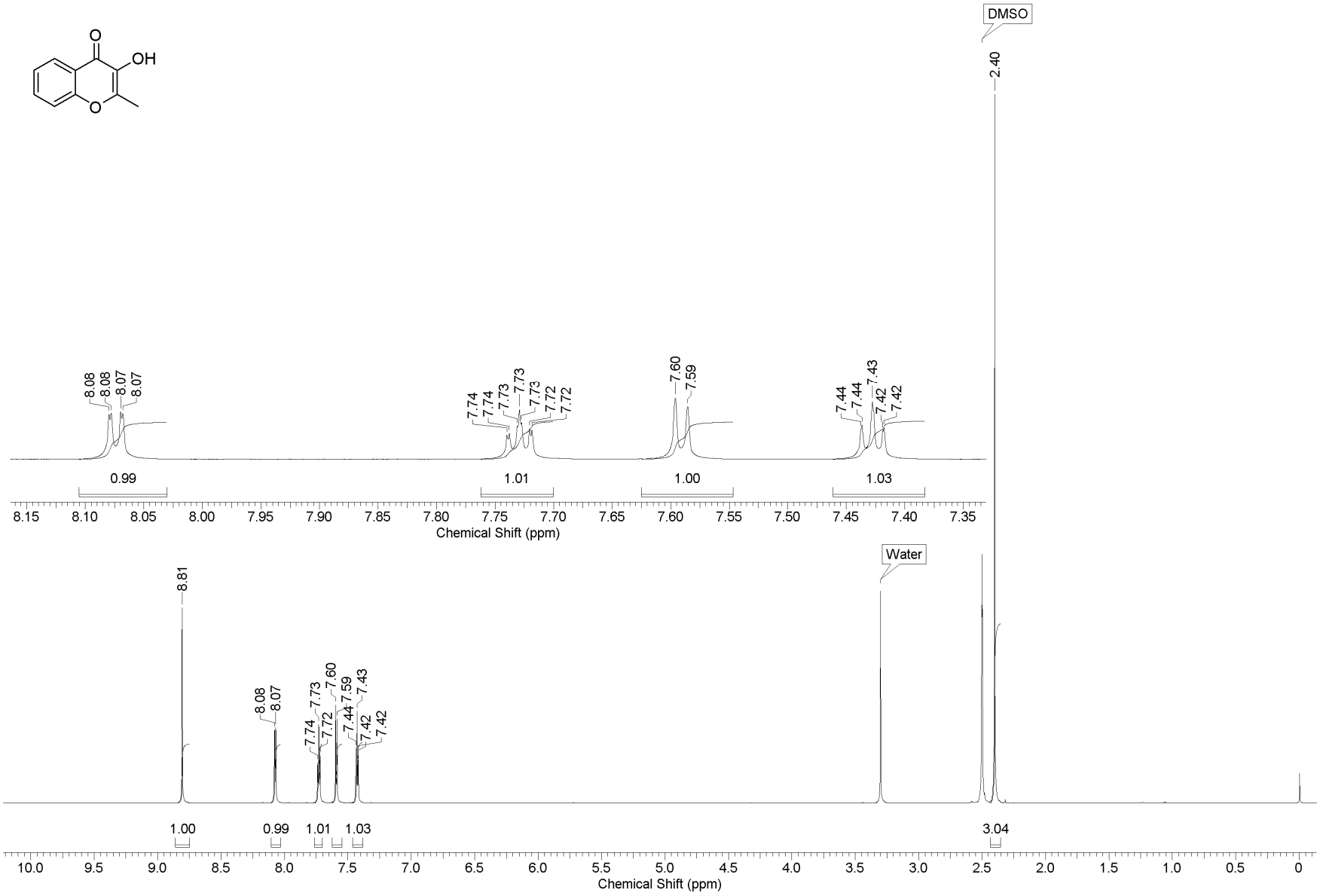

Br
O
OH
O
DMSO
171.48
154.14
141.99
141.24
135.91
126.91
124.25
121.14
116.86
Chemical Shift (ppm)
Chemical Shift (ppm)

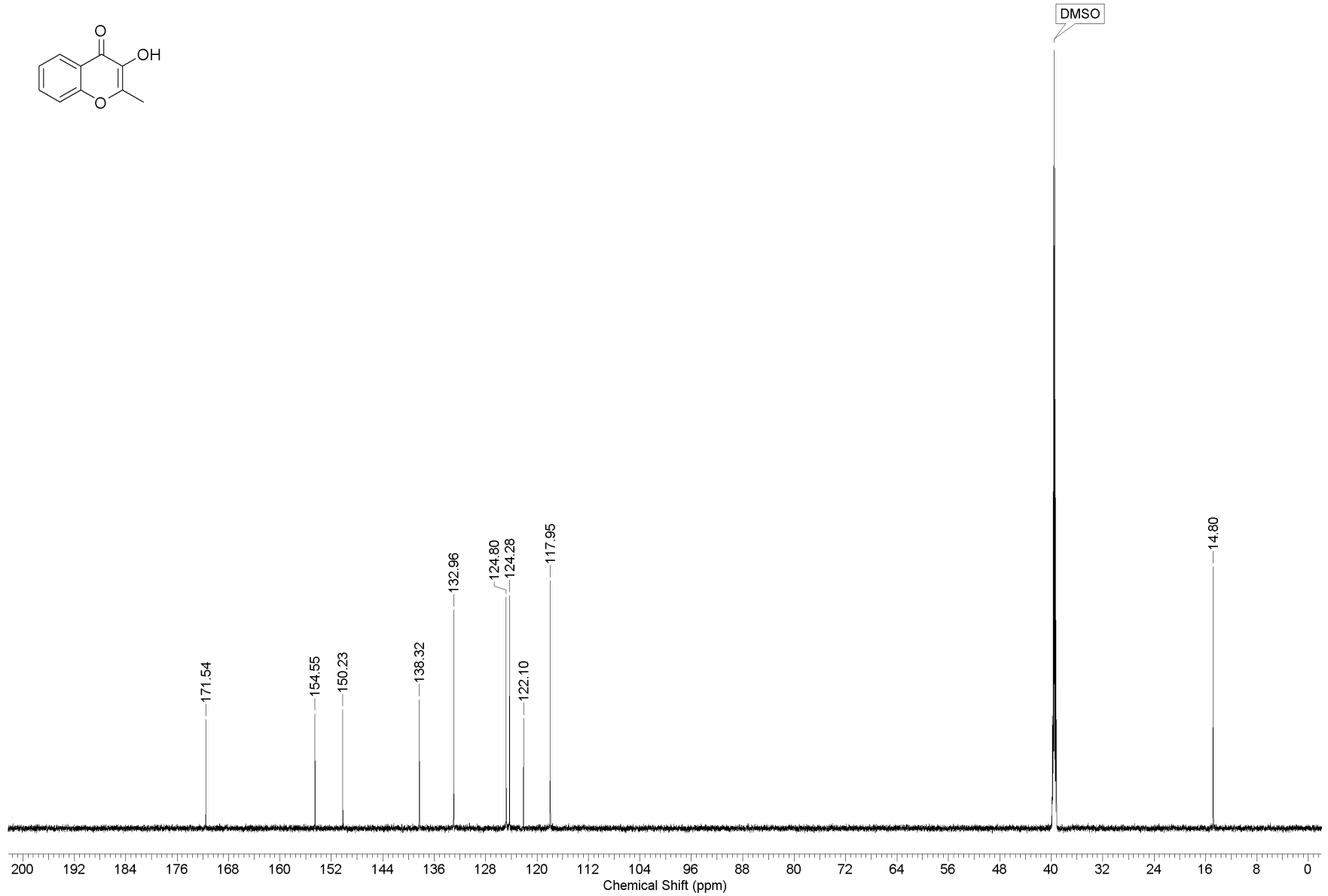

O
OH
Br
O
DMSO
8.23
8.03
8.02
7.98
7.98
7.62
7.62
7.61
7.61
1.02
1.07
1.00
1.06
8.30 8.25 8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55
Chemical Shift (ppm)
Water
9.26
8.23
8.03
8.02
7.98
7.62
7.61
1.07
1.02
1.00
1.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

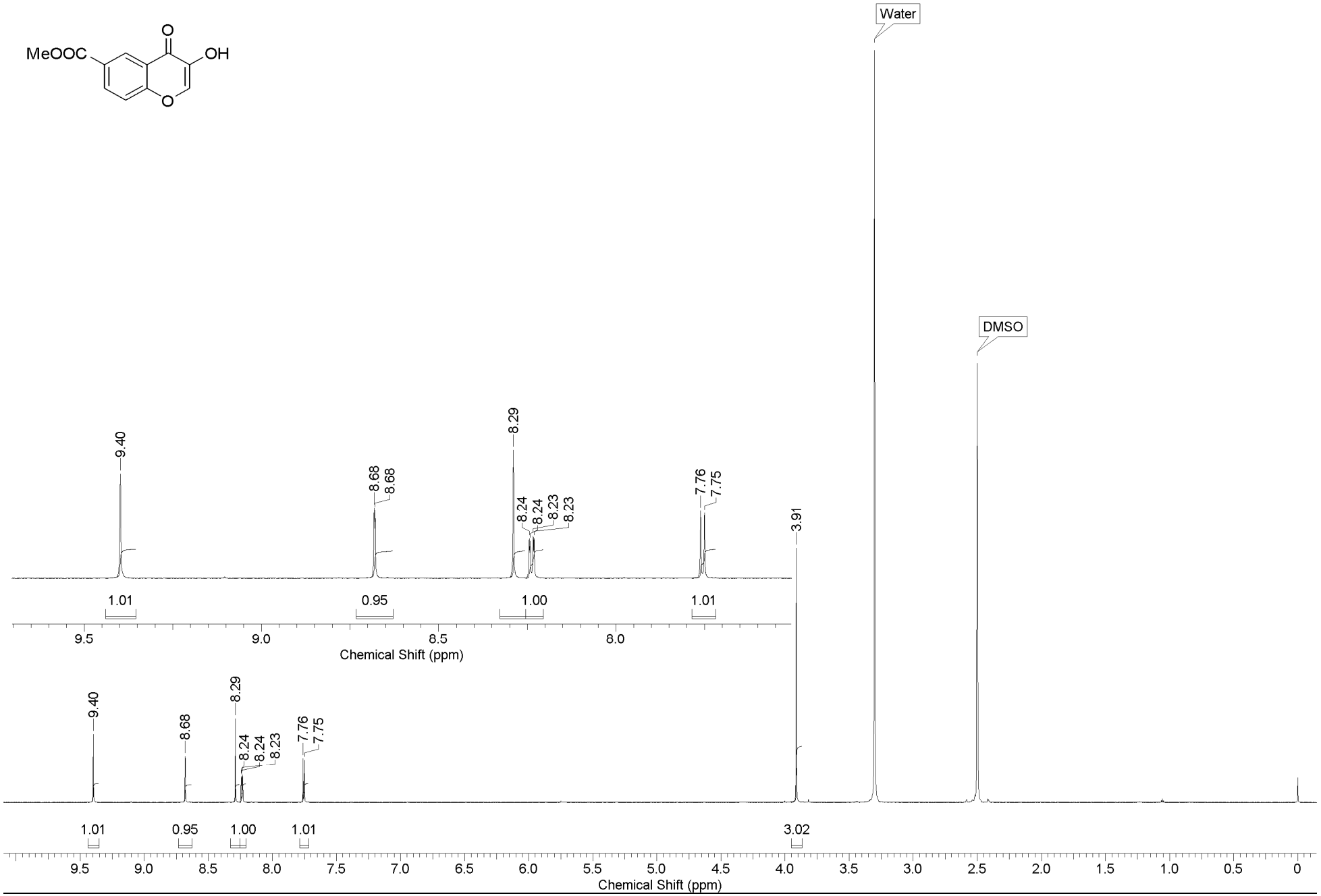

O
OH
Br
O
DMSO
142.08
140.80
127.77
126.81
126.46
121.83
121.14
Chemical Shift (ppm)
172.18
155.35
142.08
140.80
127.77
126.81
126.46
121.83
121.14
Chemical Shift (ppm)

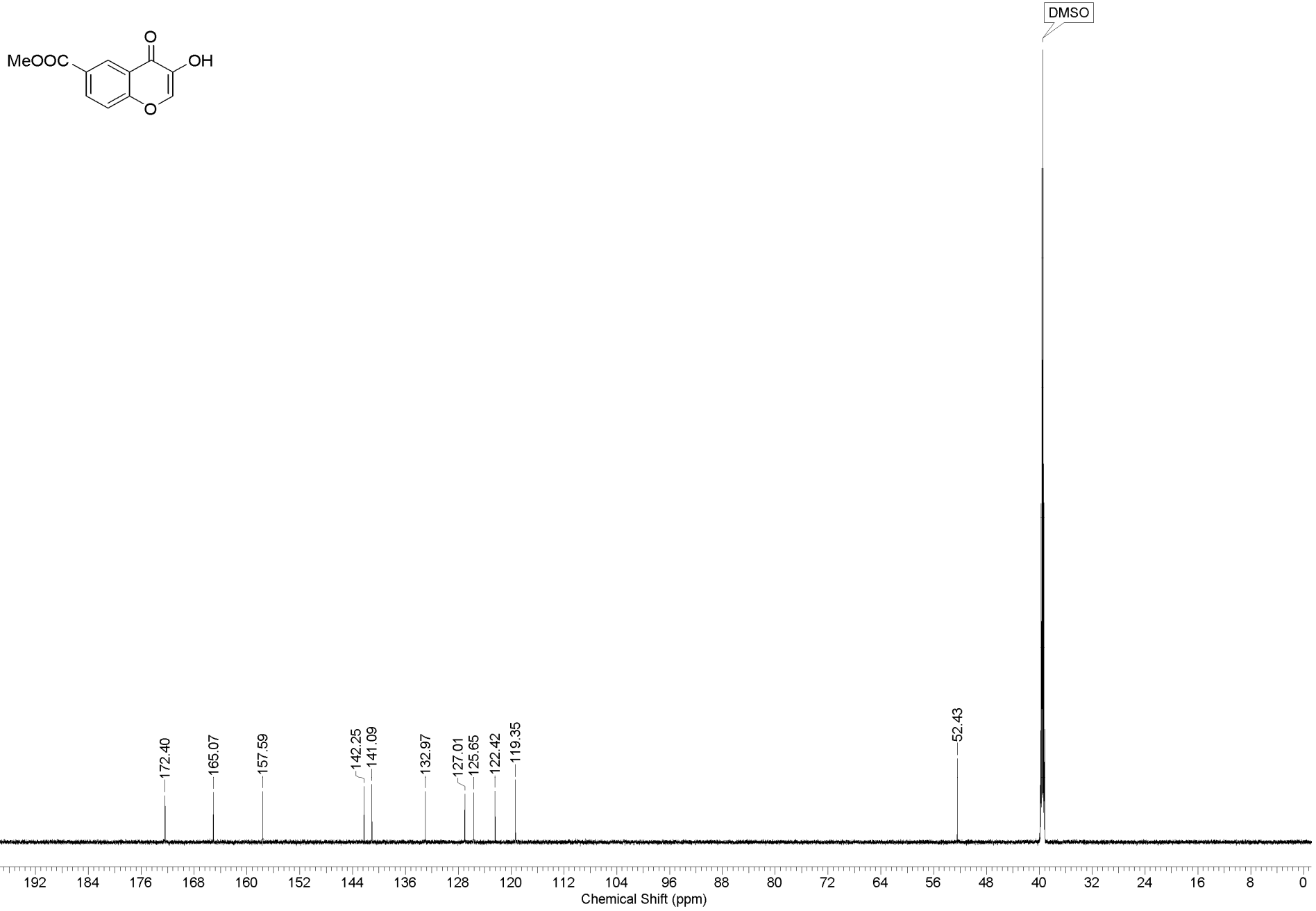

O
OH
O
OMe
DMSO
Water
8.25
7.64
7.63
7.63
7.62
7.37
7.36
7.35
7.34
0.96
1.00
2.14
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
Chemical Shift (ppm)
3.94
9.13
8.25
7.64
7.63
7.62
7.37
7.36
7.35
7.34
0.99
0.96
1.00
2.14
3.19
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

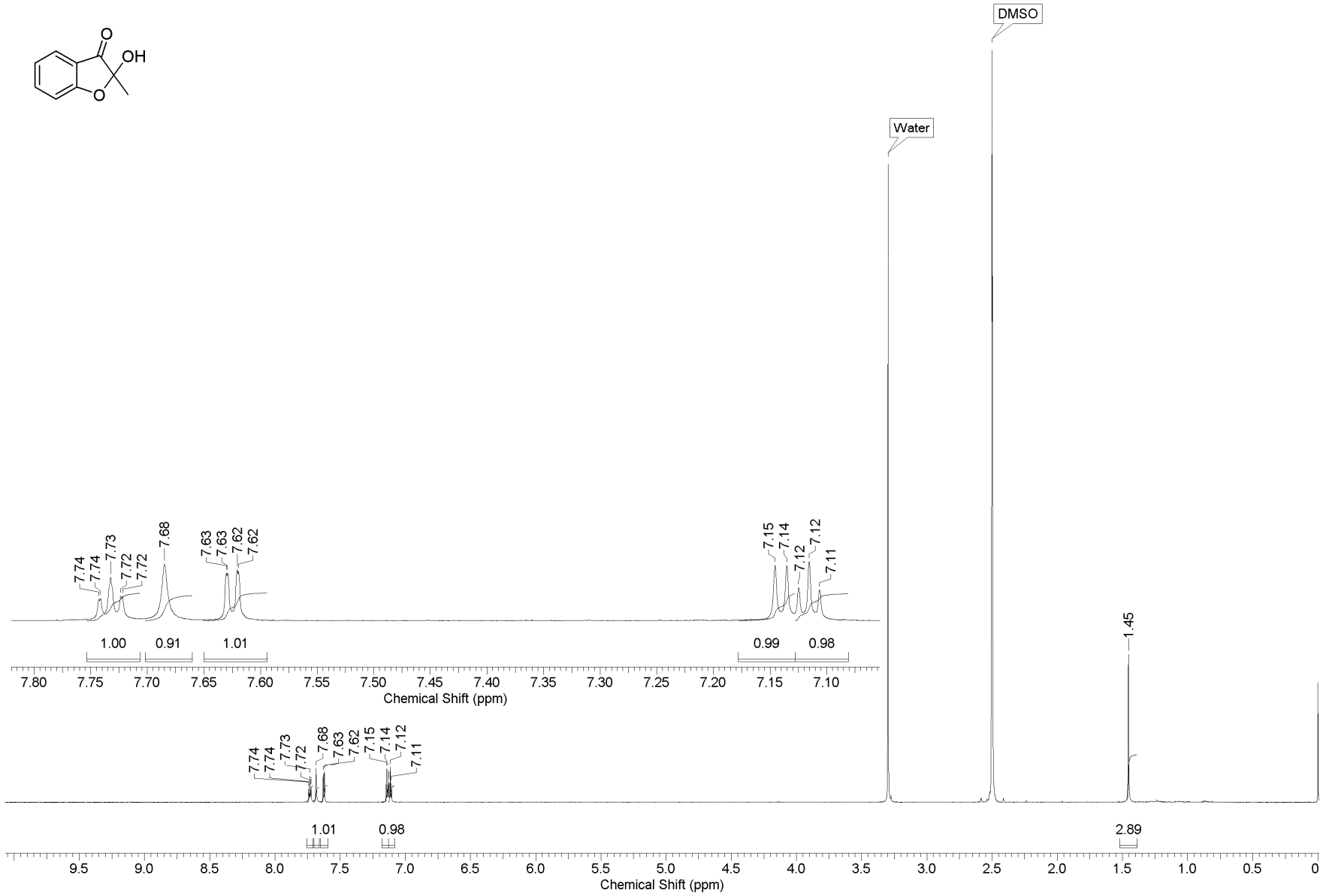

O
OH
O
OMe
DMSO
172.34
148.61
145.66
141.74
140.15
124.08
123.59
115.32
113.88
56.05
Chemical Shift (ppm)
Chemical Shift (ppm)

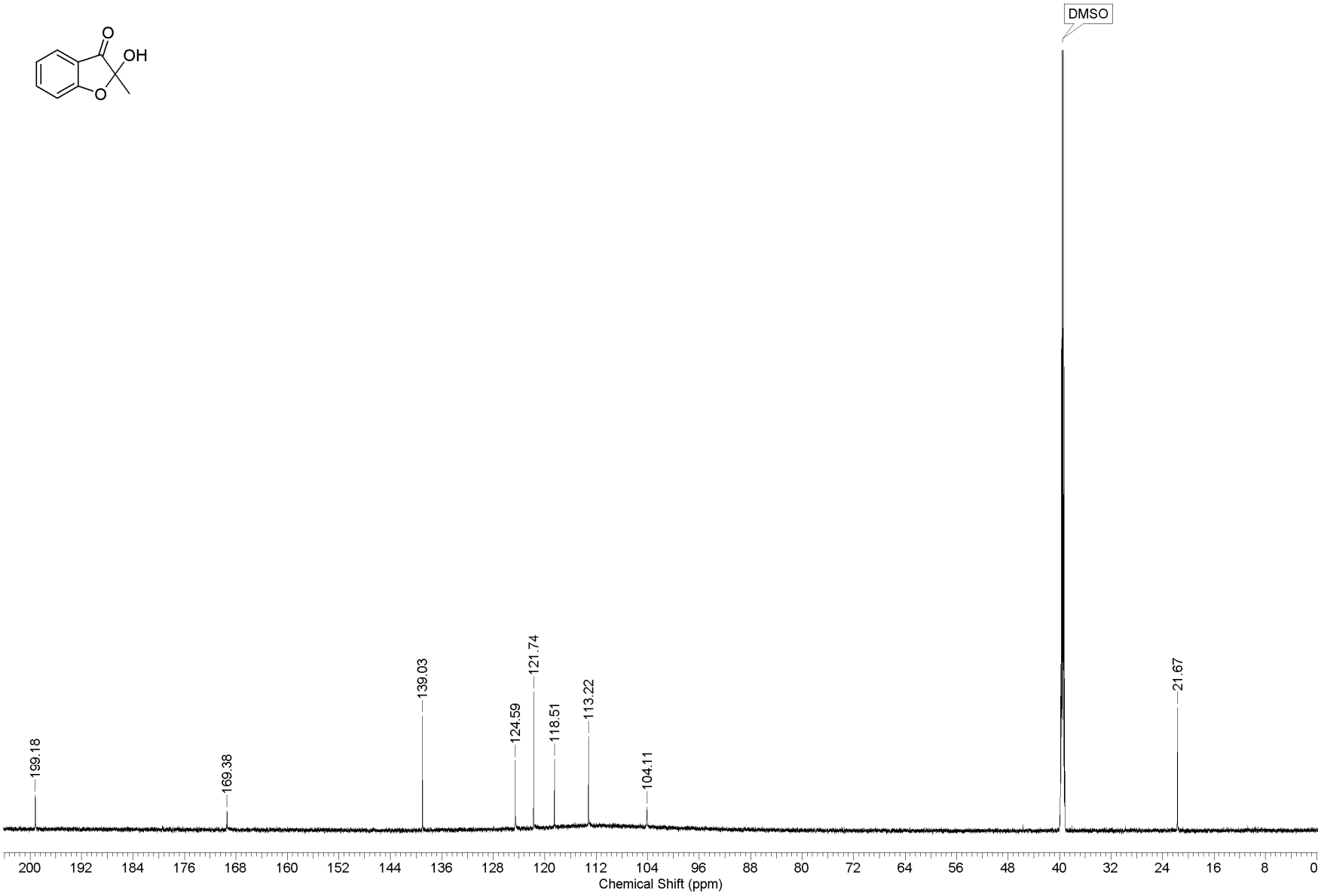

O
OH
O
DMSO
2.40
8.08
8.08
8.07
8.07
7.74
7.74
7.73
7.73
7.73
7.72
7.72
7.60
7.59
7.44
7.44
7.43
7.42
7.42
0.99
1.01
1.00
1.03
8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35
Chemical Shift (ppm)
Water
8.81
8.08
8.07
7.74
7.73
7.72
7.60
7.59
7.44
7.43
7.42
7.42
1.00
0.99
1.01
1.03
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

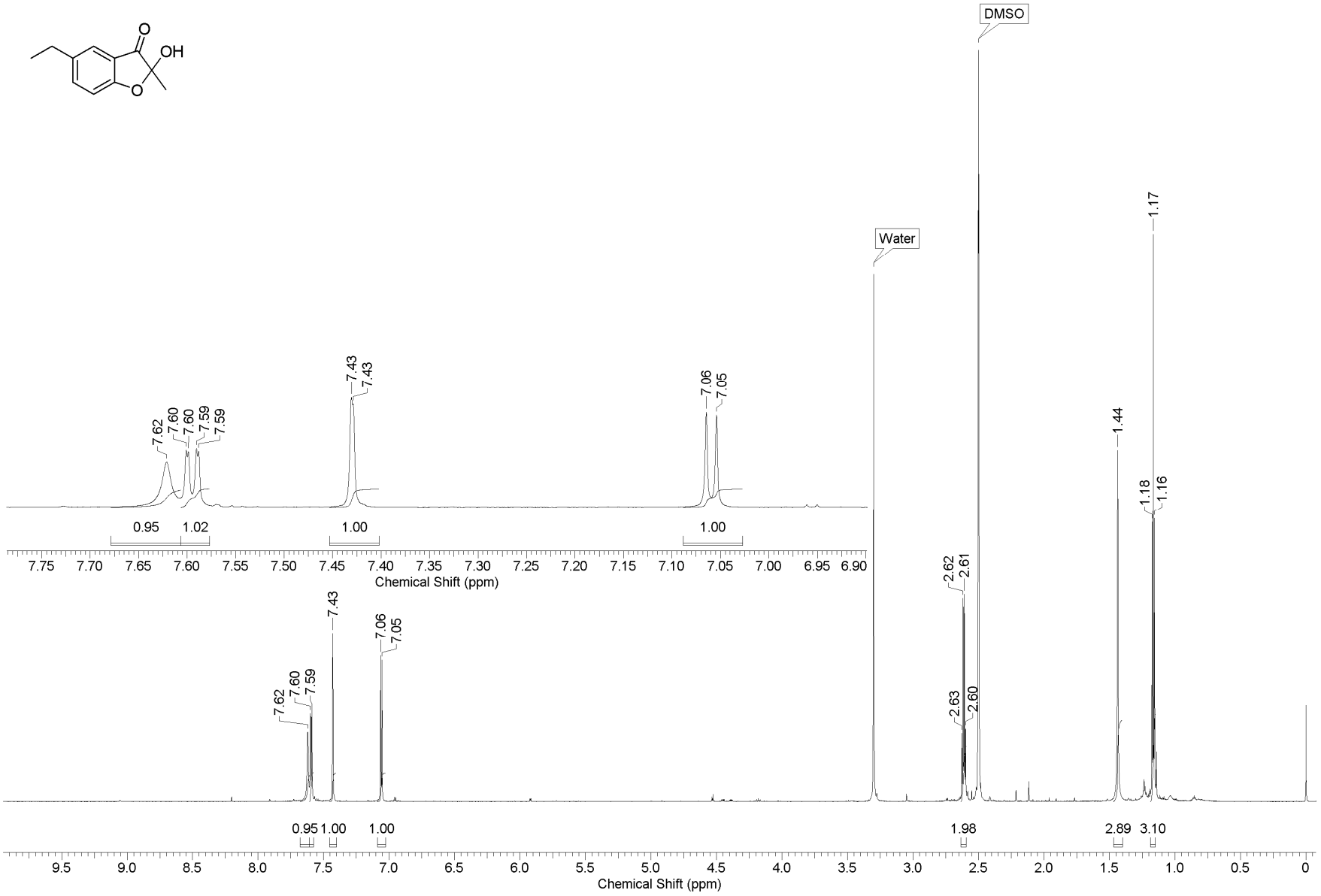

O
OH
O
DMSO
171.54
154.55
150.23
138.32
132.96
124.80
124.28
122.10
117.95
14.80
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

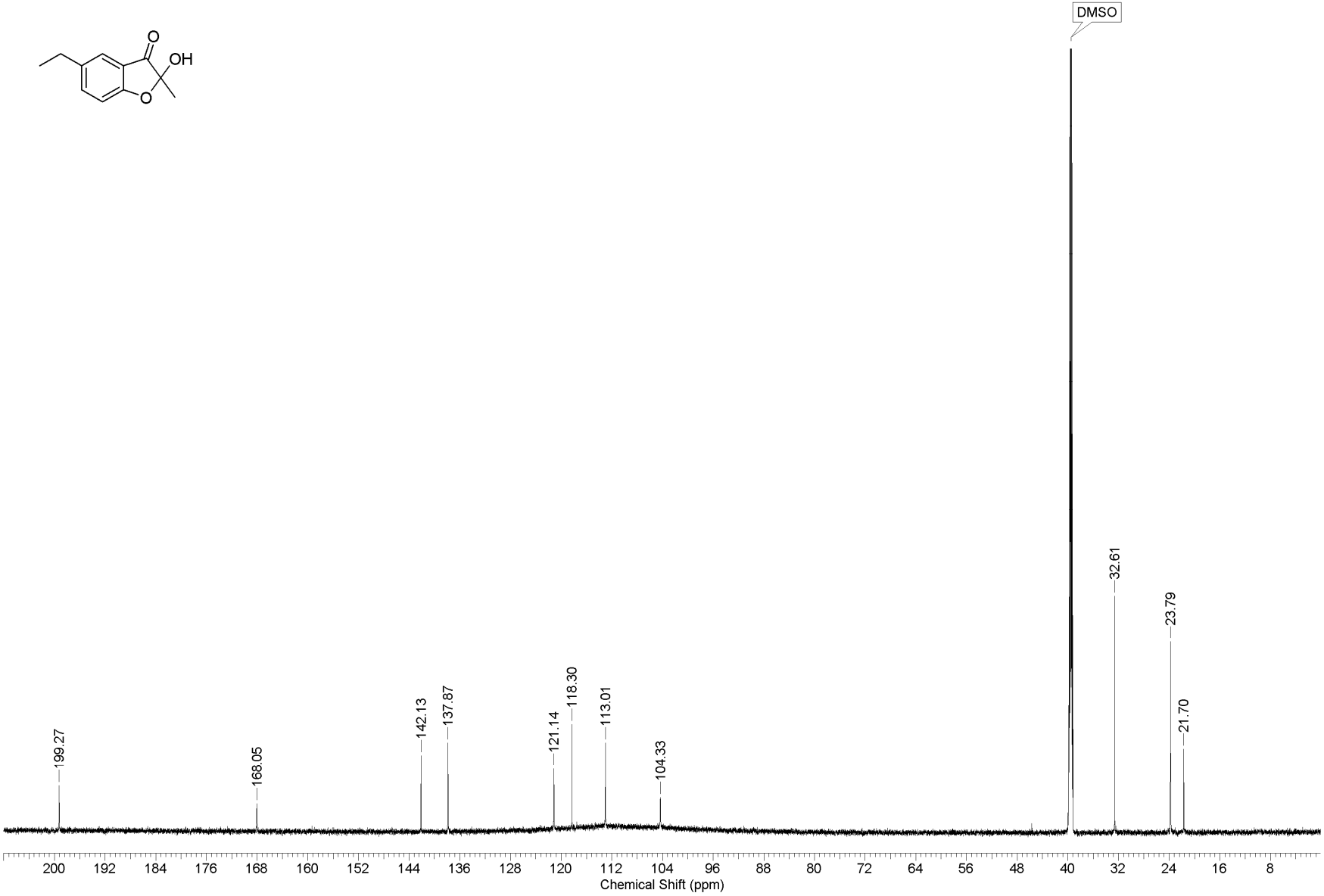

MeOOC
O
OH
O
Water
DMSO
9.40
8.68
8.68
8.29
8.24
8.24
8.23
8.23
7.76
7.75
3.91
1.01
0.95
1.00
1.01
3.02
Chemical Shift (ppm)

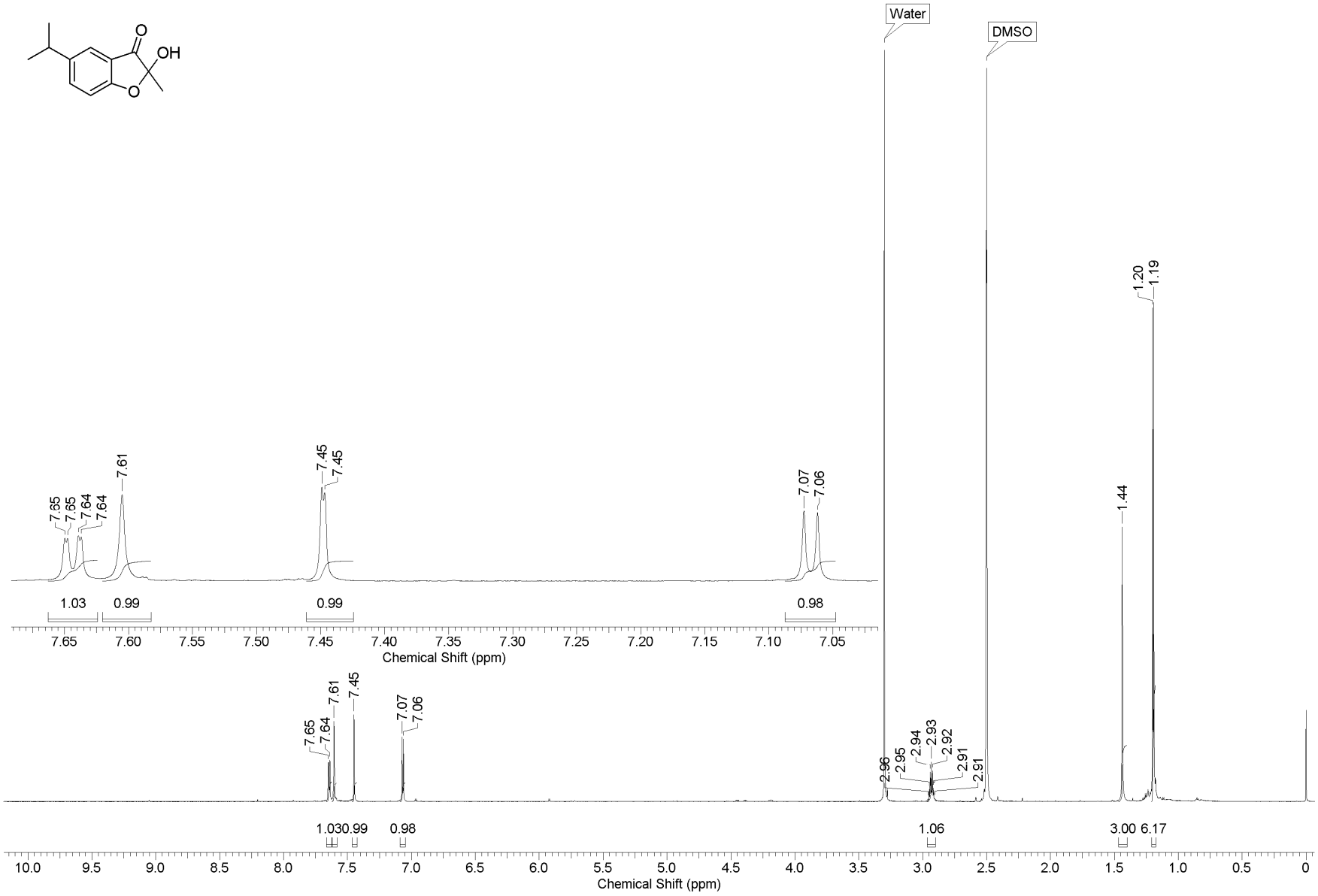

MeOOC
O
OH
O
DMSO
172.40
165.07
157.59
142.25
141.09
132.97
127.01
125.65
122.42
119.35
52.43
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

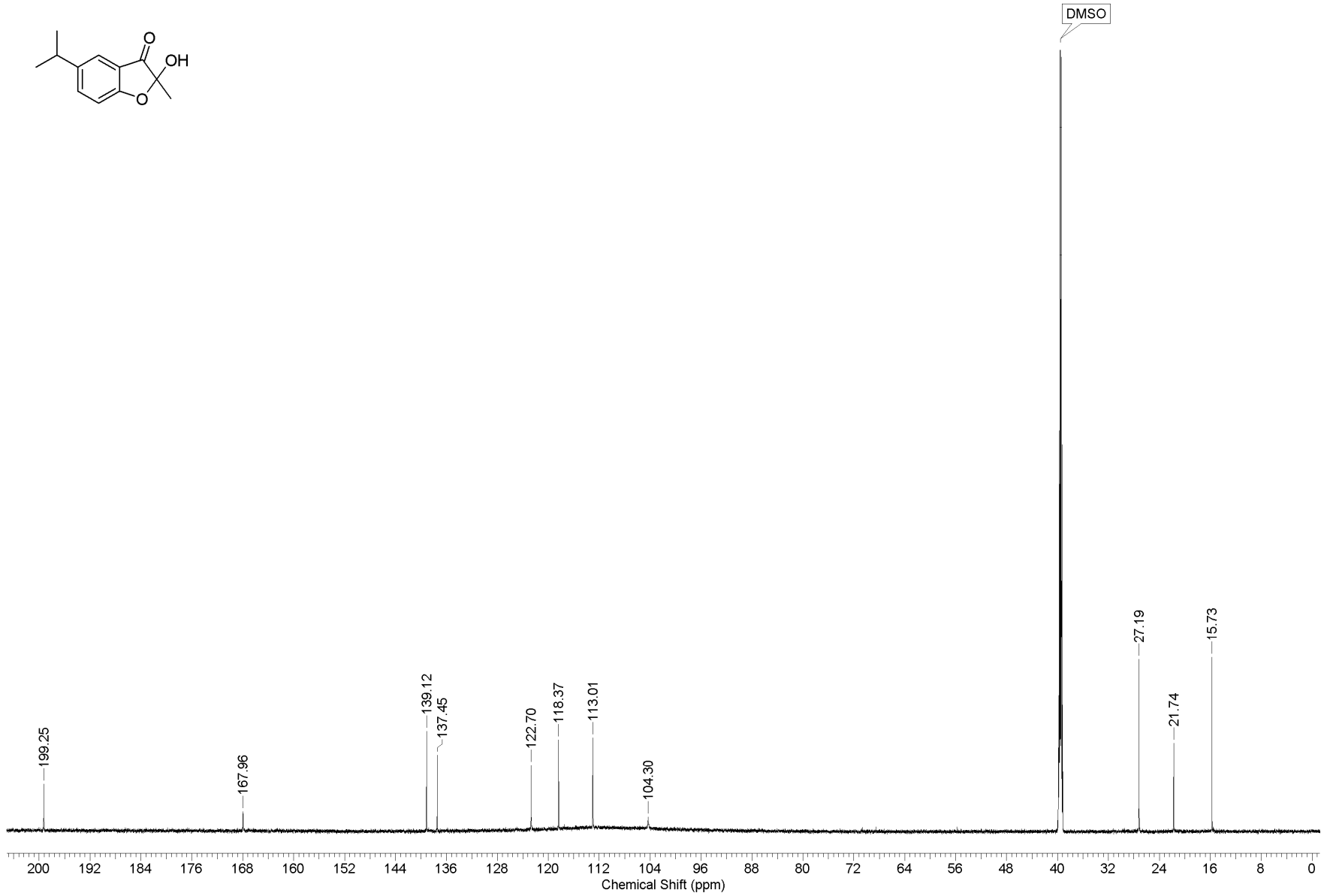

O
OH
O
DMSO
Water
7.74
7.74
7.73
7.72
7.72
7.68
7.63
7.63
7.62
7.62
7.15
7.14
7.12
7.12
7.11
1.45
1.00
0.91
1.01
0.99
0.98
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
Chemical Shift (ppm)
1.01
0.98
2.89
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

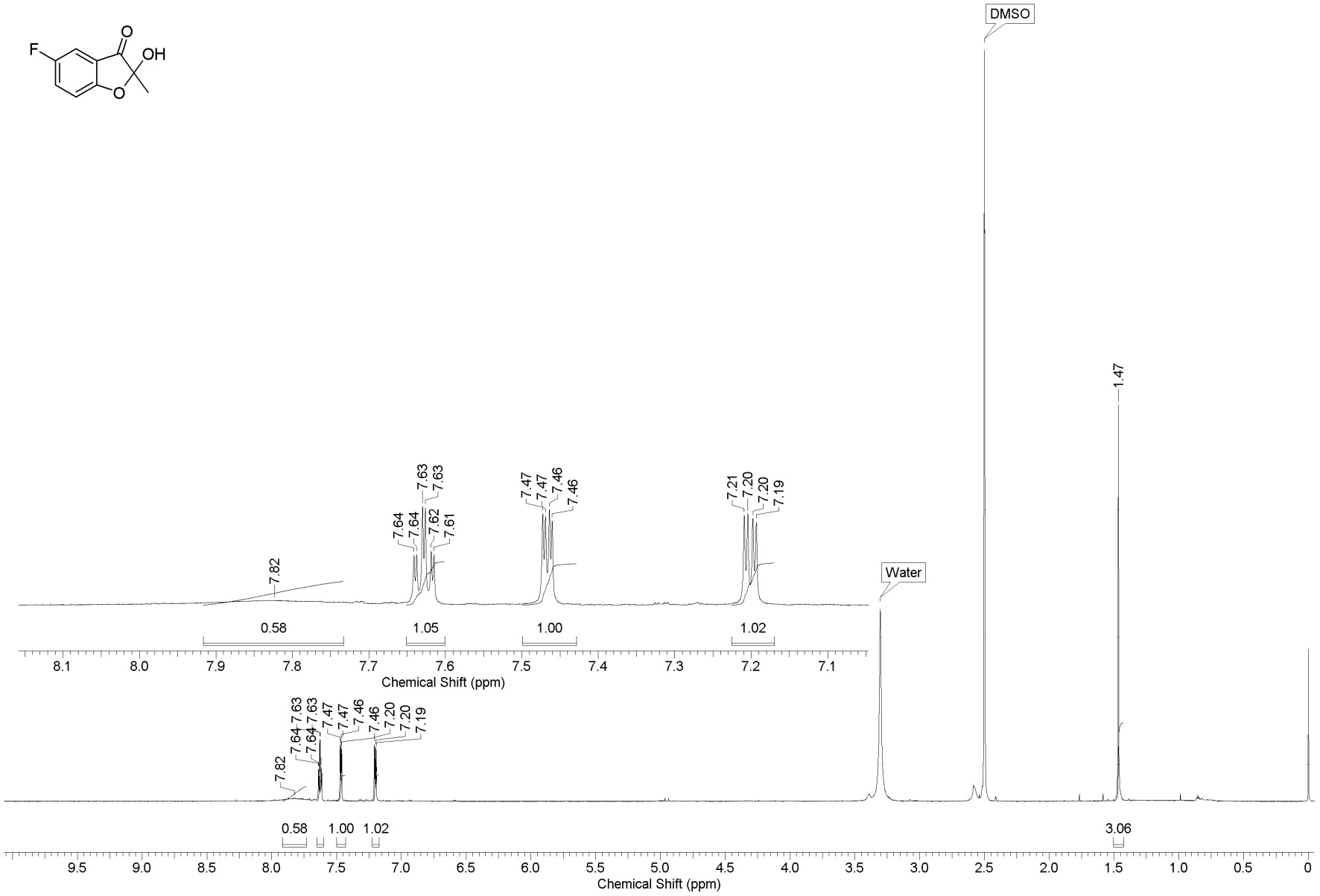

O
OH
O
DMSO
199.18
169.38
139.03
124.59
121.74
118.51
113.22
104.11
21.67
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

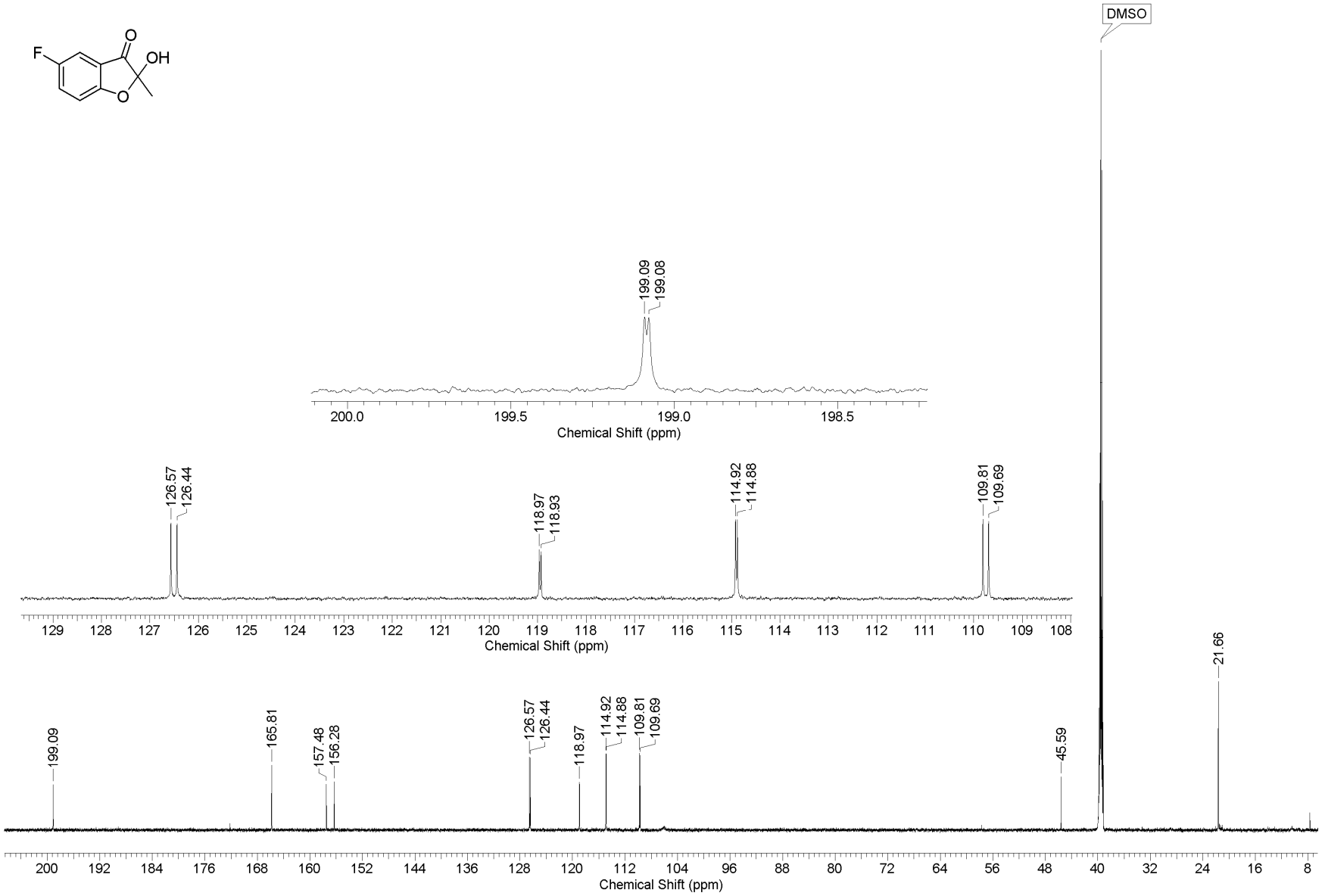

O
OH
O
DMSO
Water
7.62
7.60
7.60
7.59
7.59
7.43
7.43
7.06
7.05
1.44
1.17
1.18
1.16
2.62
2.61
2.63
2.60
0.95
1.02
1.00
1.00
1.98
2.89
3.10
Chemical Shift (ppm)
Chemical Shift (ppm)

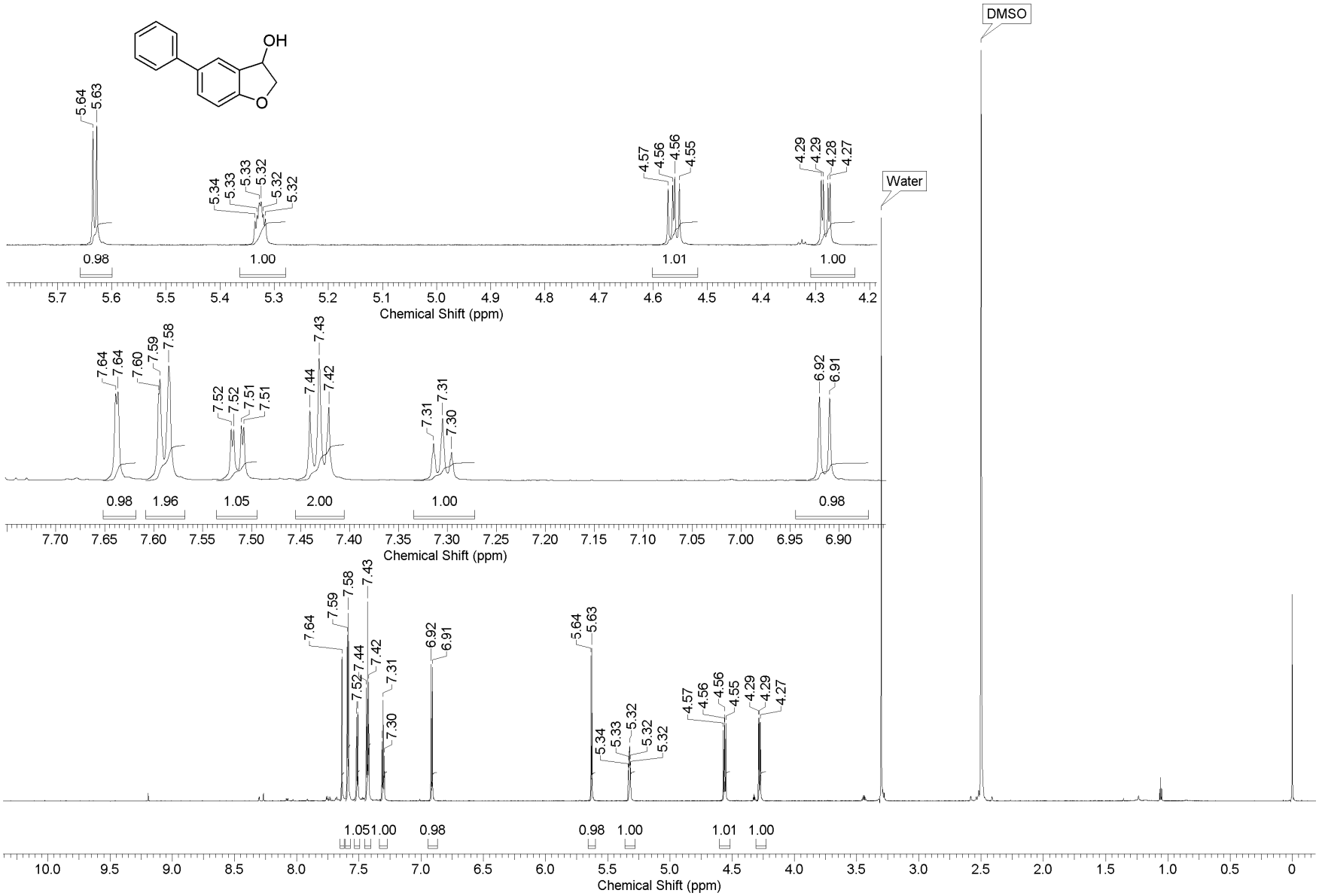

O
OH
O
DMSO
199.27
168.05
142.13
137.87
121.14
118.30
113.01
104.33
32.61
23.79
21.70
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)

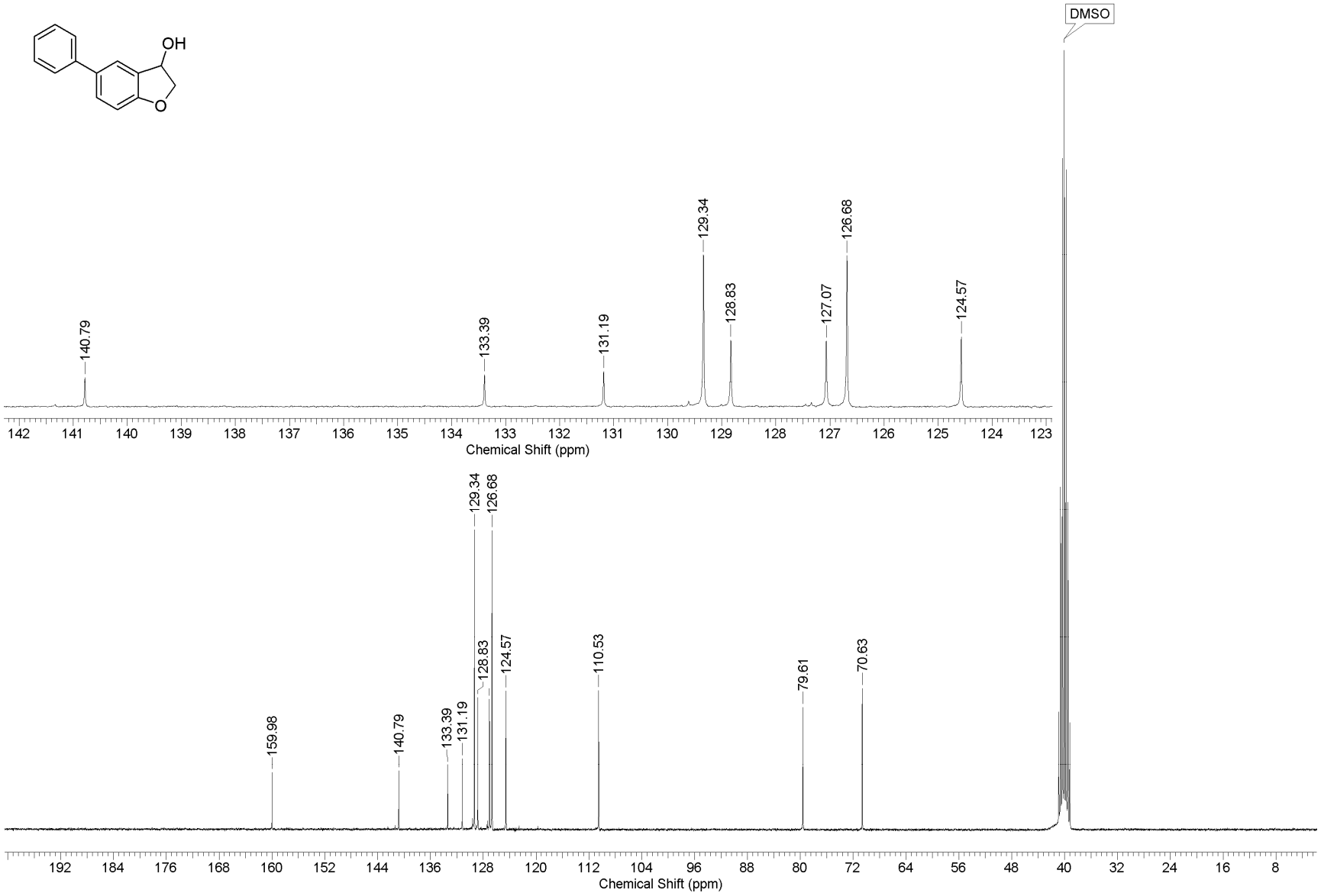

O
OH
O
Water
DMSO
7.65
7.65
7.64
7.64
7.61
7.45
7.45
7.07
7.06
1.20
1.19
1.44
1.03
0.99
0.99
0.98
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
Chemical Shift (ppm)
7.65
7.64
7.61
7.45
7.07
7.06
2.96
2.95
2.94
2.93
2.92
2.91
2.91
1.03
0.99
0.98
1.06
3.00
6.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

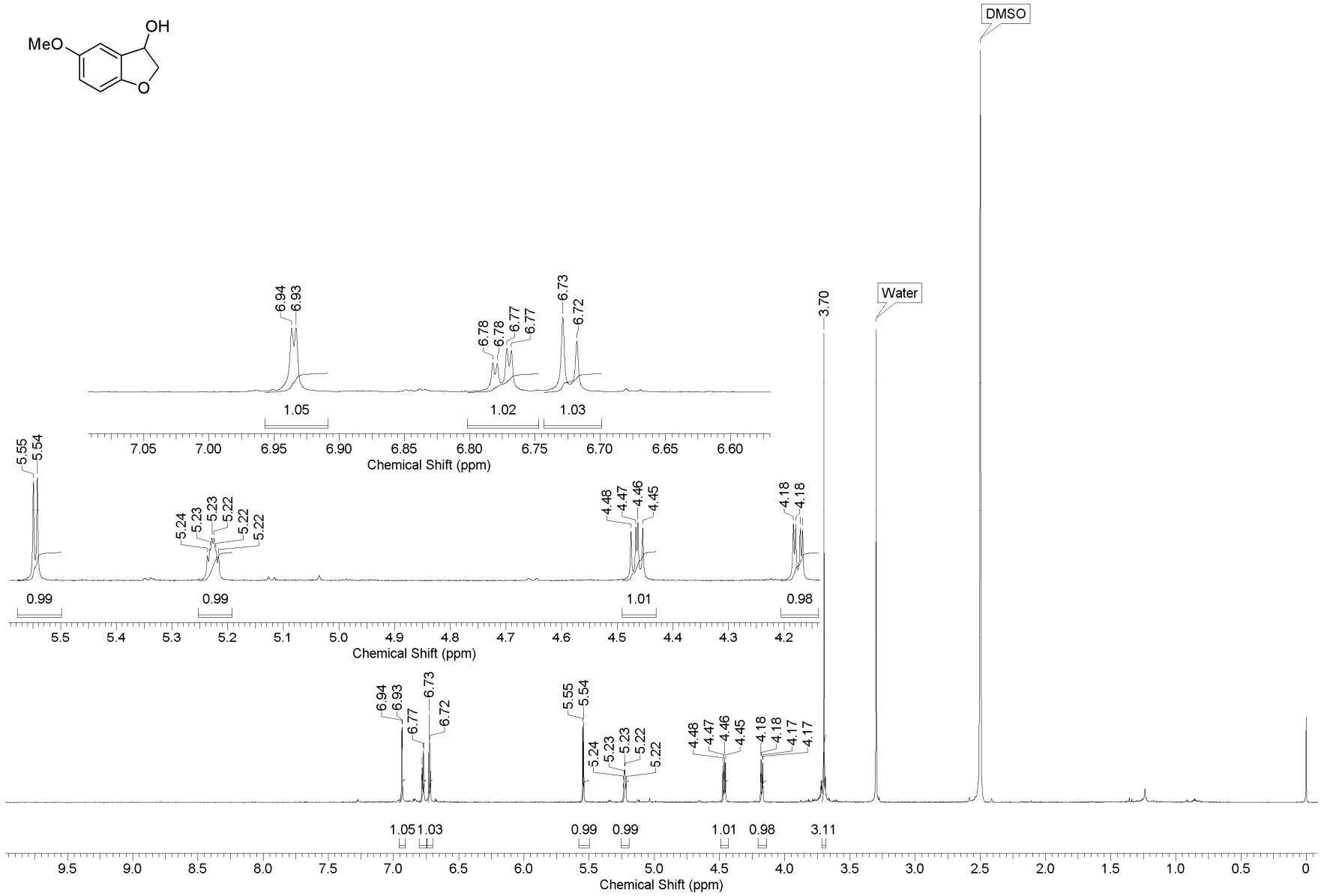

O
OH
O
DMSO
199.25
167.96
139.12
137.45
122.70
118.37
113.01
104.30
27.19
21.74
15.73
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

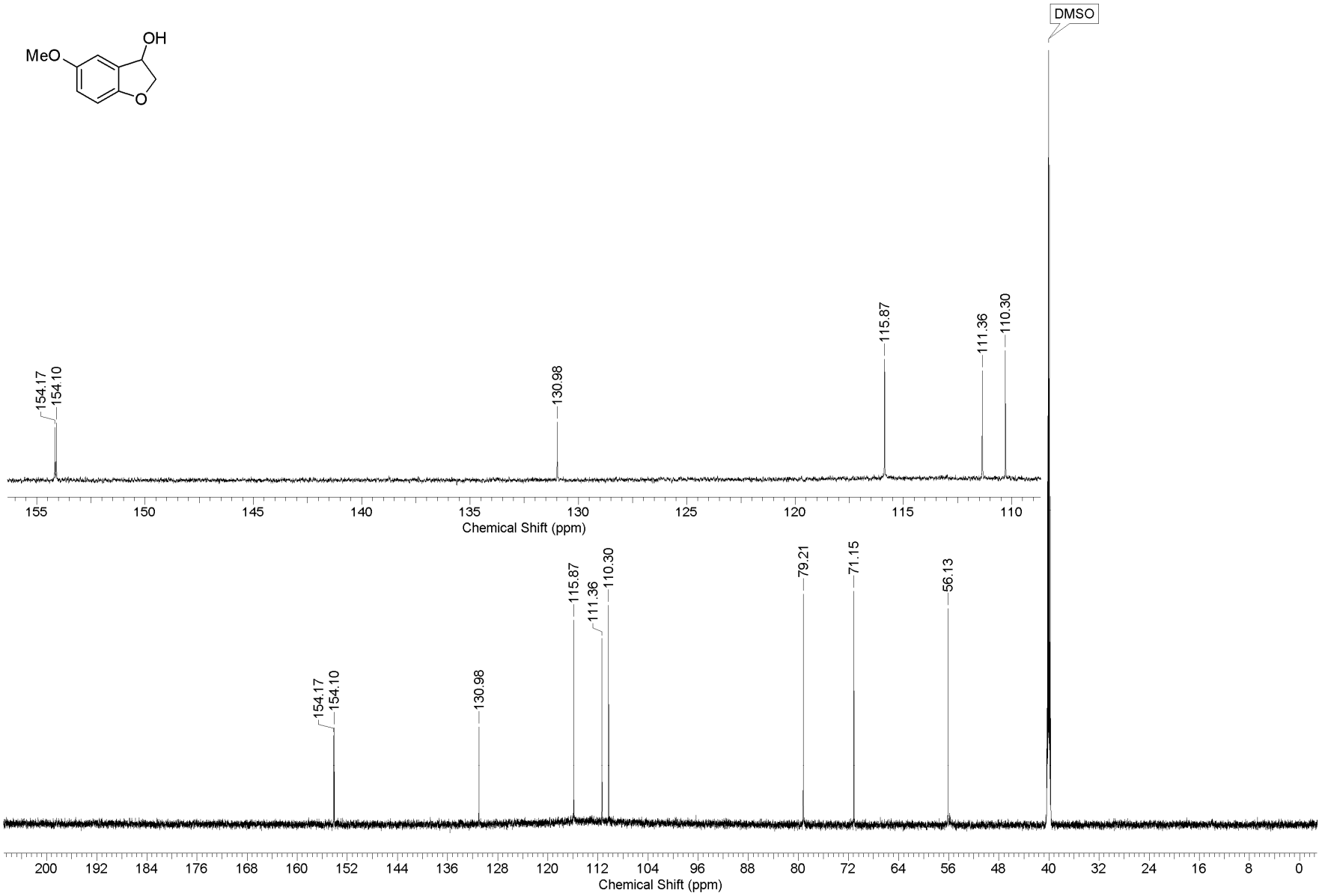

F
O
OH
O
DMSO
Water
1.47
7.82
7.64
7.64
7.63
7.63
7.62
7.61
7.47
7.47
7.46
7.46
7.21
7.20
7.20
7.19
0.58
1.05
1.00
1.02
Chemical Shift (ppm)
3.06
Chemical Shift (ppm)

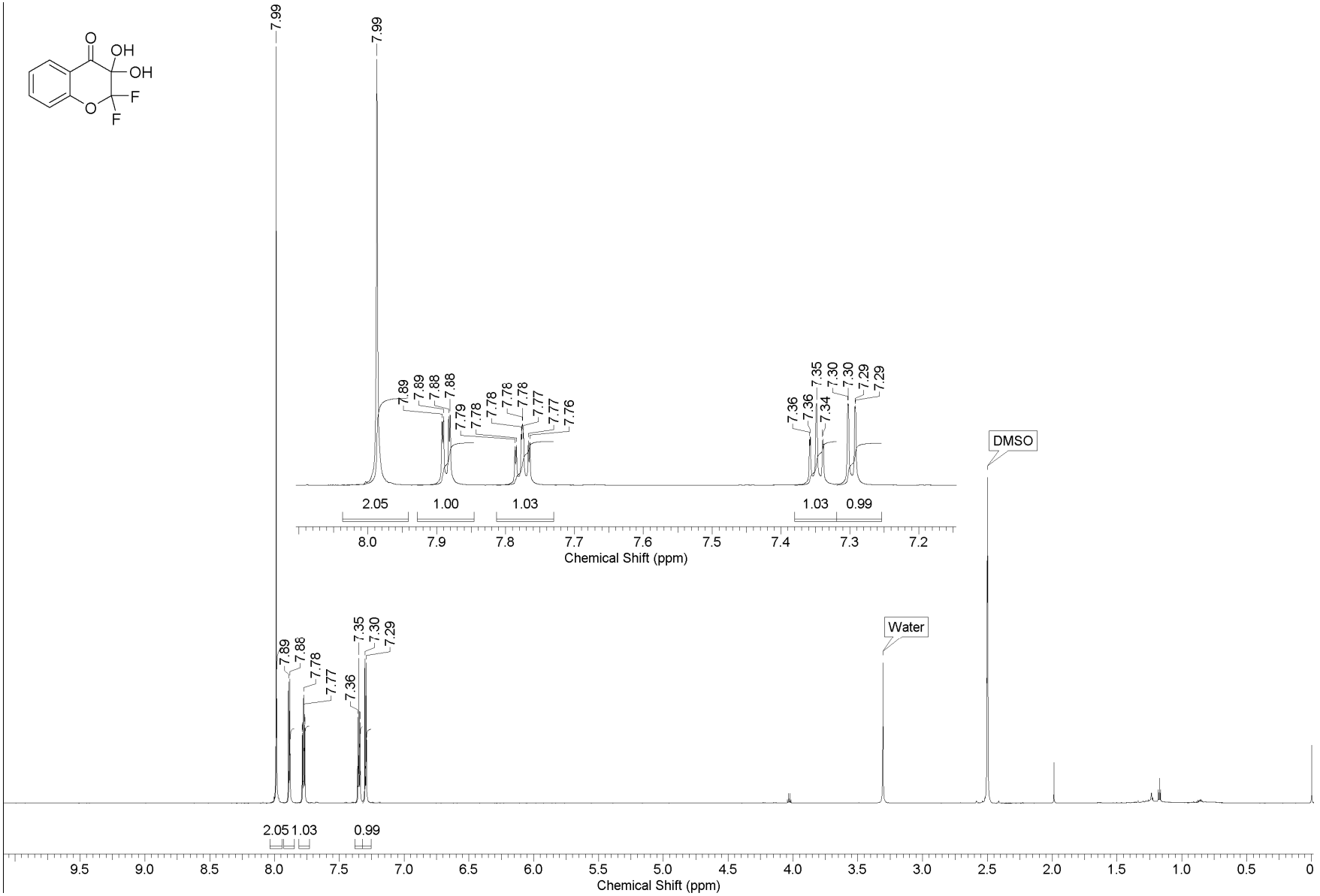

F
O
OH
O
DMSO
199.09
199.08
200.0
199.5
199.0
198.5
Chemical Shift (ppm)
126.57
126.44
118.97
118.93
114.92
114.88
109.81
109.69
129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114 113 112 111 110 109 108
Chemical Shift (ppm)
21.66
199.09
165.81
157.48
156.28
126.57
126.44
118.97
114.92
114.88
109.81
109.69
45.59
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)

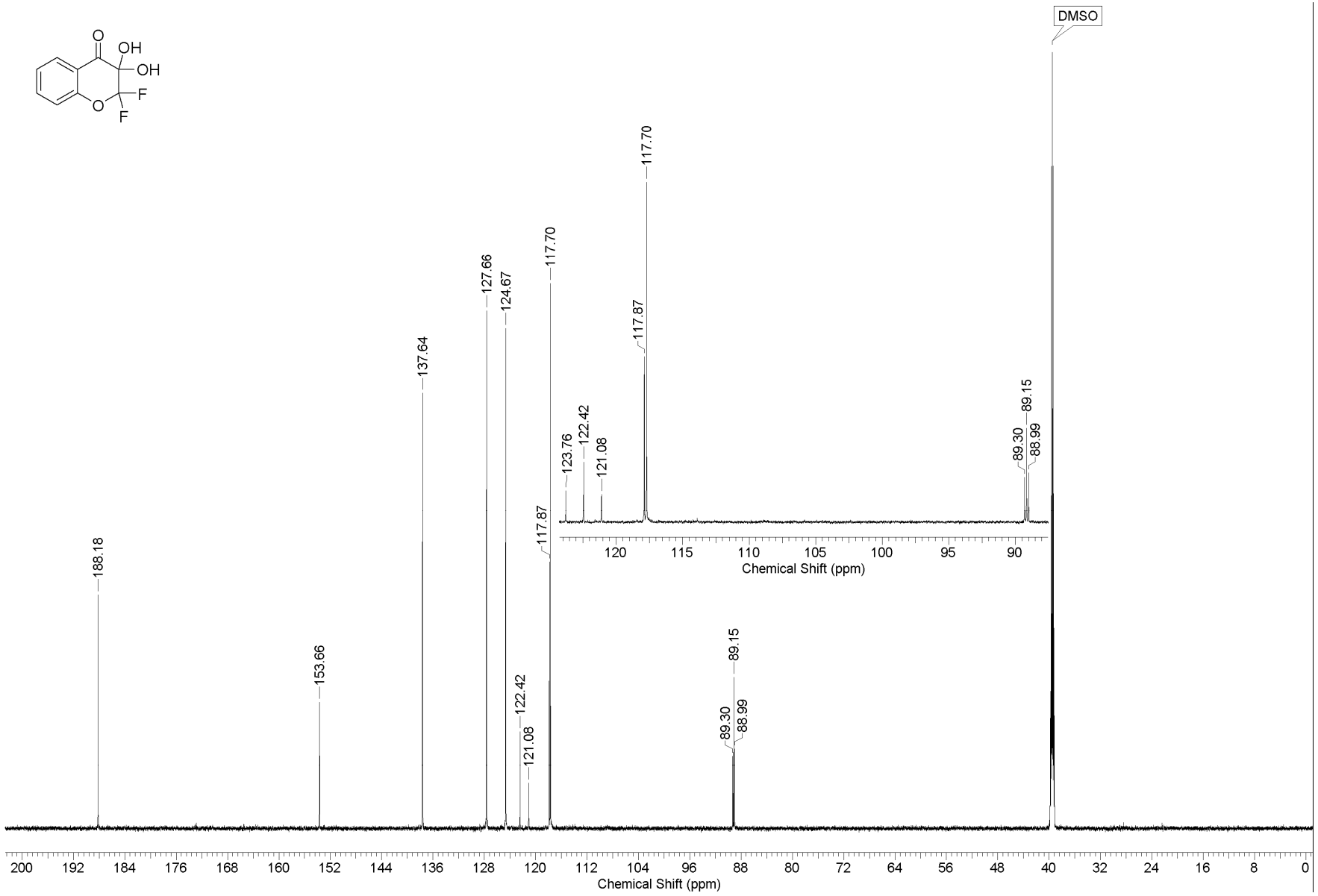

OH
O
DMSO
Water
5.64
5.63
5.34
5.33
5.33
5.32
5.32
5.32
4.57
4.56
4.56
4.55
4.29
4.29
4.28
4.27
0.98
1.00
1.01
1.00
Chemical Shift (ppm)
7.64
7.64
7.60
7.59
7.58
7.52
7.52
7.51
7.51
7.44
7.43
7.42
7.31
7.31
7.30
6.92
6.91
0.98
1.96
1.05
2.00
1.00
0.98
Chemical Shift (ppm)
7.64
7.59
7.58
7.43
7.52
7.44
7.42
7.31
7.30
6.92
6.91
5.64
5.63
5.34
5.33
5.32
5.32
5.32
4.57
4.56
4.56
4.55
4.29
4.29
4.27
1.05
1.00
0.98
0.98
1.00
1.01
1.00
Chemical Shift (ppm)

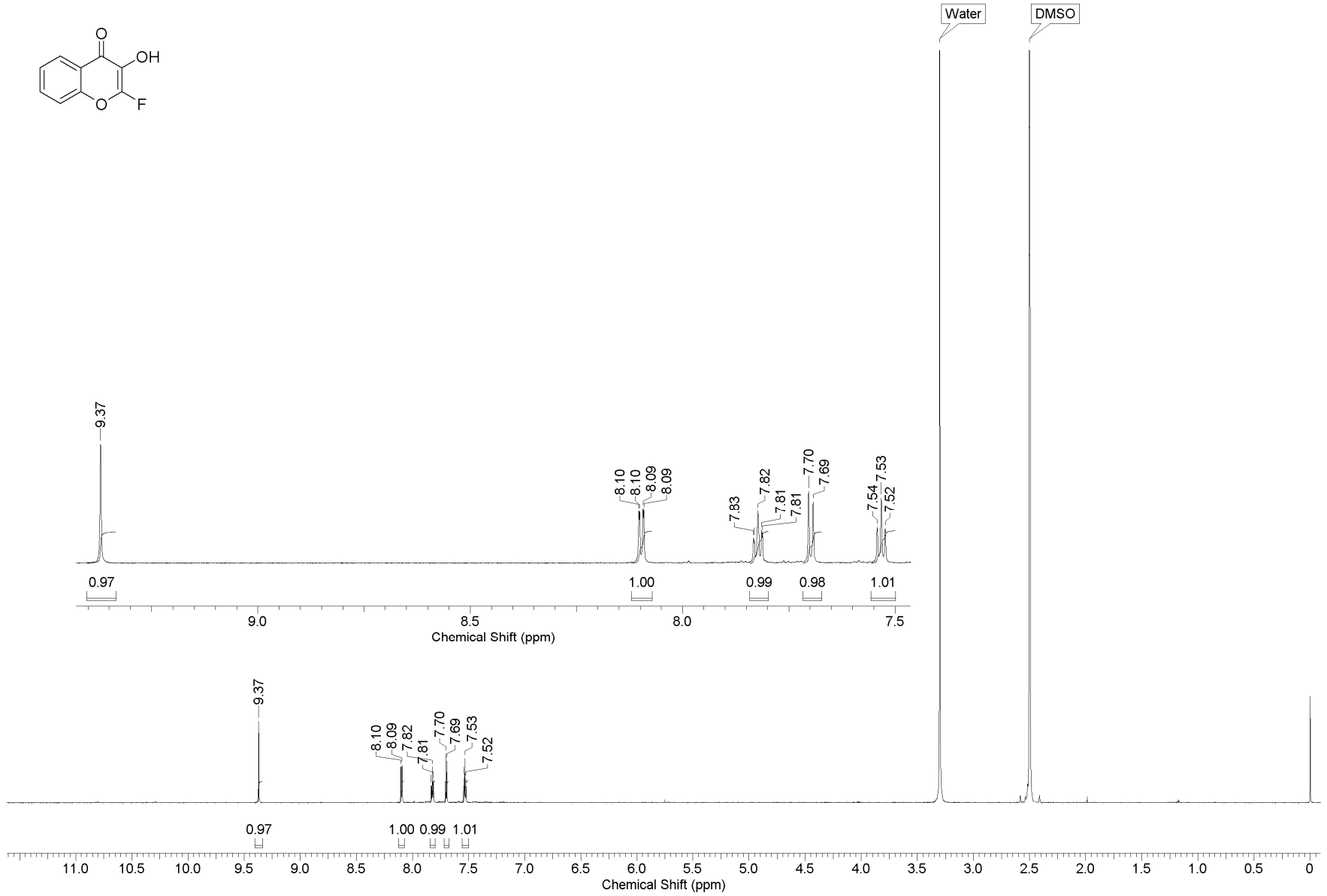

OH
O
DMSO
140.79
133.39
131.19
129.34
128.83
127.07
126.68
124.57
Chemical Shift (ppm)
159.98
140.79
133.39
131.19
129.34
126.68
128.83
124.57
110.53
79.61
70.63
Chemical Shift (ppm)

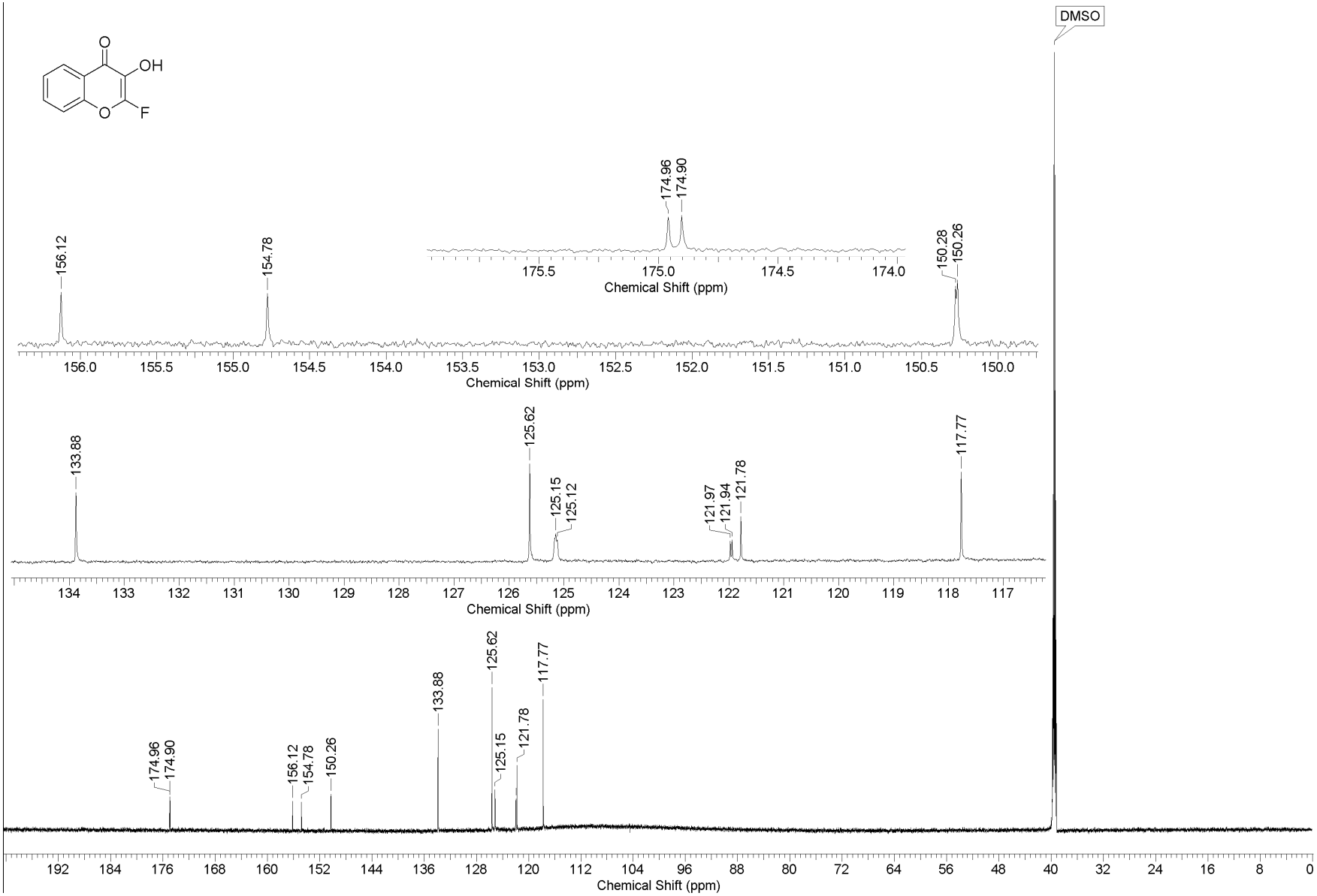

MeO
OH
O
DMSO
Water
6.94
6.93
6.78
6.78
6.77
6.77
6.73
6.72
3.70
5.55
5.54
5.24
5.23
5.23
5.22
5.22
5.22
4.48
4.47
4.46
4.45
4.18
4.18
1.05
1.02
1.03
0.99
0.99
1.01
0.98
Chemical Shift (ppm)
6.94
6.93
6.77
6.73
6.72
5.55
5.54
5.24
5.23
5.22
5.22
4.48
4.47
4.46
4.45
4.18
4.18
4.17
4.17
1.05
1.03
0.99
0.99
1.01
0.98
3.11
Chemical Shift (ppm)

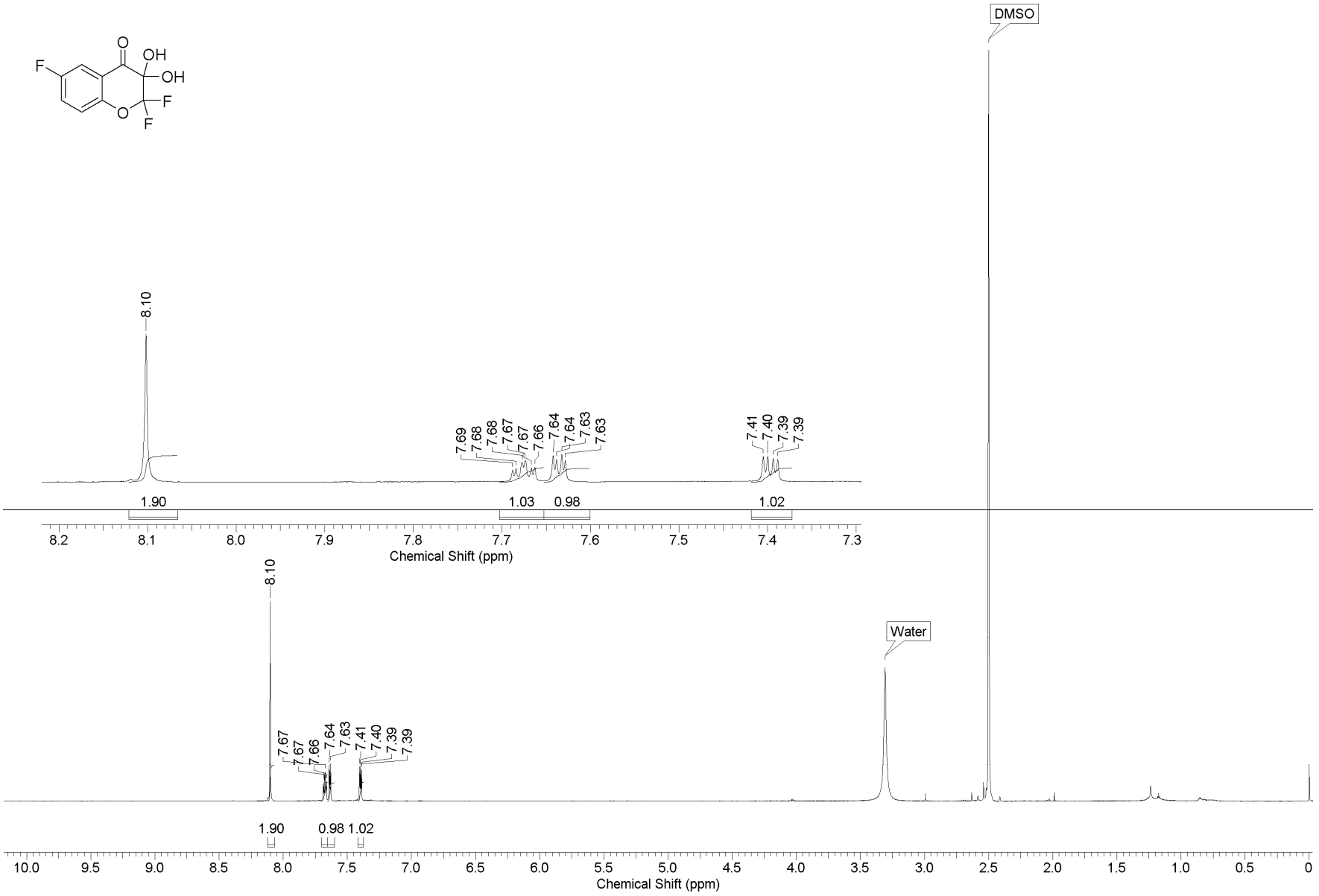

MeO
OH
O
DMSO
154.17
154.10
130.98
115.87
111.36
110.30
79.21
71.15
56.13
Chemical Shift (ppm)
Chemical Shift (ppm)

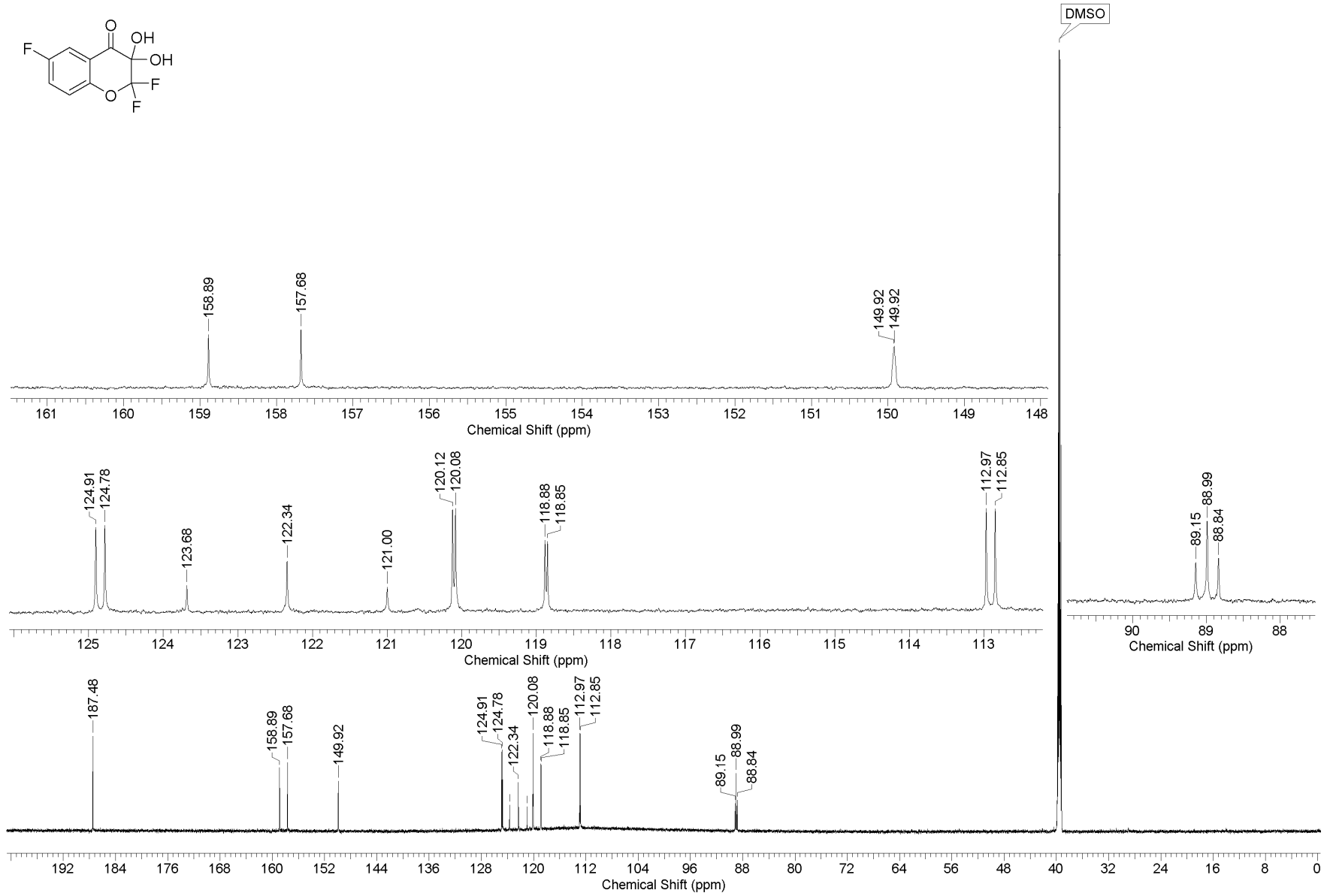

O
OH
OH
F
F
O
7.99
7.99
7.89
7.89
7.88
7.88
7.79
7.78
7.78
7.78
7.78
7.77
7.77
7.76
7.36
7.36
7.35
7.34
7.30
7.30
7.29
7.29
2.05
1.00
1.03
1.03
0.99
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
Chemical Shift (ppm)
DMSO
Water
7.89
7.88
7.78
7.77
7.36
7.35
7.30
7.29
2.05
1.03
0.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

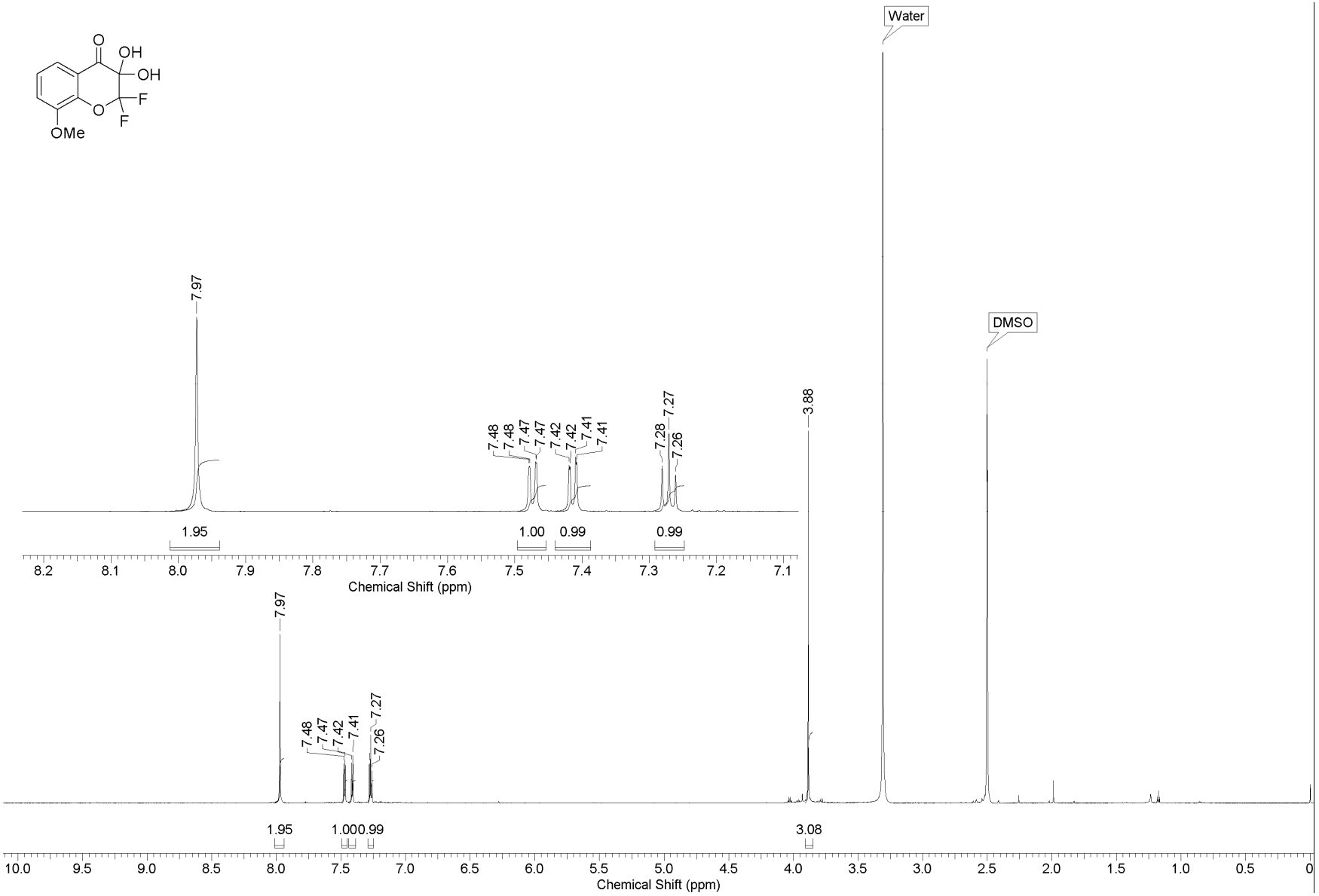

O
OH
OH
F
F
O
DMSO
188.18
153.66
137.64
127.66
124.67
122.42
121.08
117.87
117.70
89.30
88.99
89.15
123.76
Chemical Shift (ppm)
Chemical Shift (ppm)

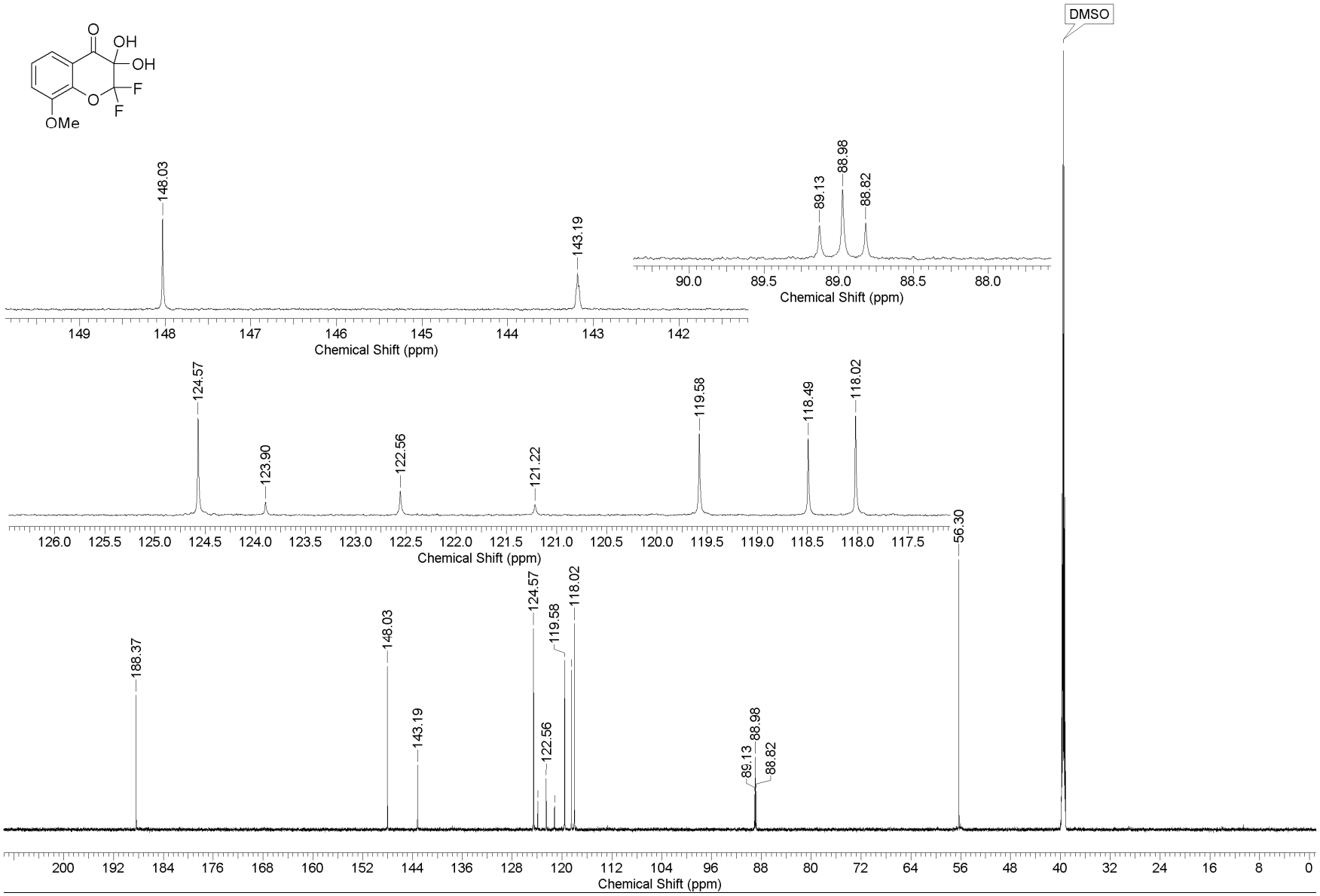

O
OH
O
F
Water
DMSO
9.37
8.10
8.10
8.09
8.09
7.83
7.82
7.81
7.81
7.70
7.69
7.54
7.53
7.52
0.97
1.00
0.99
0.98
1.01
9.0
8.5
8.0
7.5
Chemical Shift (ppm)
9.37
8.10
8.09
7.82
7.81
7.70
7.69
7.53
7.52
0.97
1.00
0.99
1.01
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

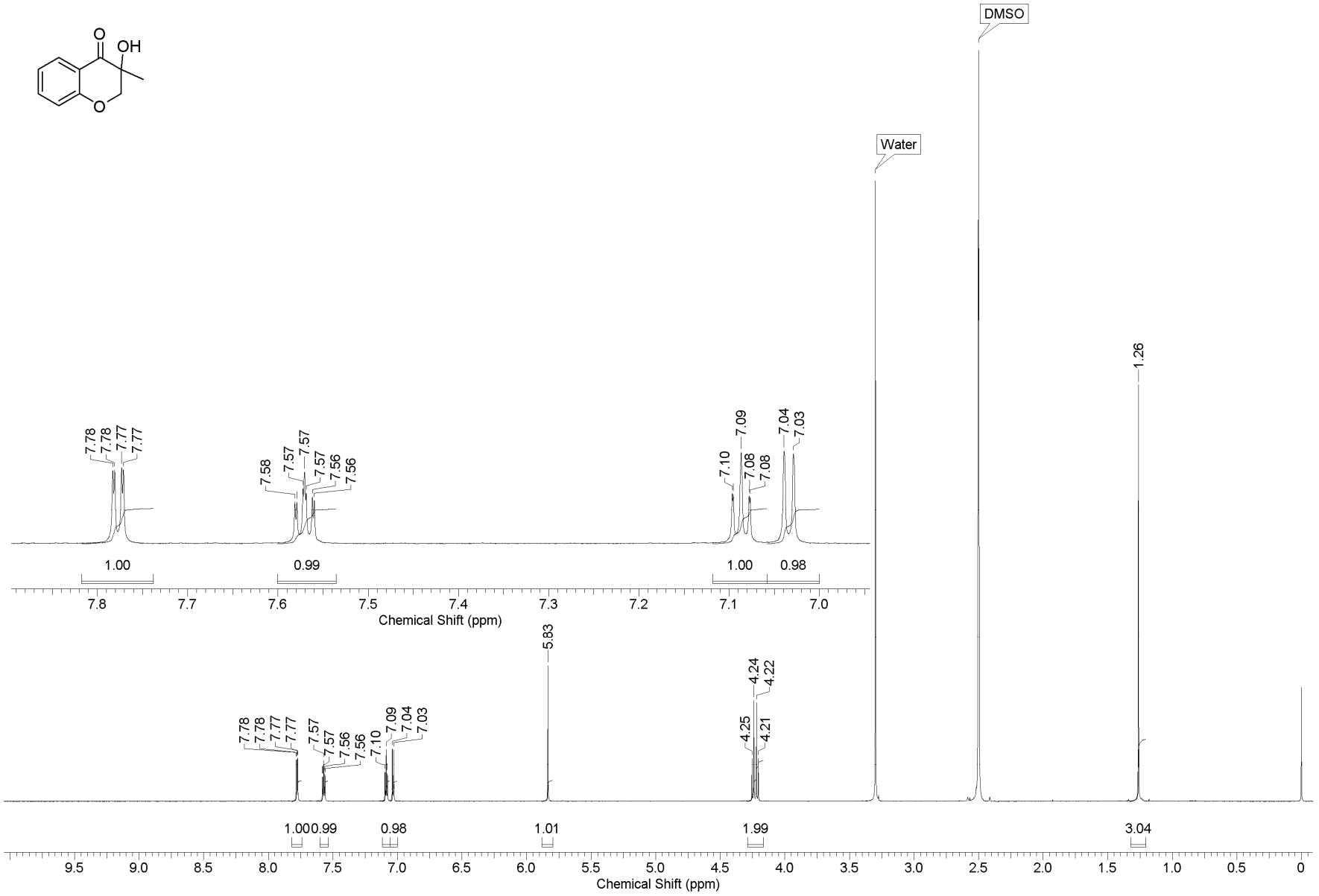

O
OH
O
F
DMSO
174.96
174.90
156.12
154.78
150.28
150.26
175.5
175.0
174.5
174.0
Chemical Shift (ppm)
156.0
155.5
155.0
154.5
154.0
153.5
153.0
152.5
152.0
151.5
151.0
150.5
150.0
Chemical Shift (ppm)
133.88
125.62
125.15
125.12
121.97
121.94
121.78
117.77
134
133
132
131
130
129
128
127
126
125
124
123
122
121
120
119
118
117
Chemical Shift (ppm)
174.96
174.90
156.12
154.78
150.26
133.88
125.62
125.15
121.78
117.77
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

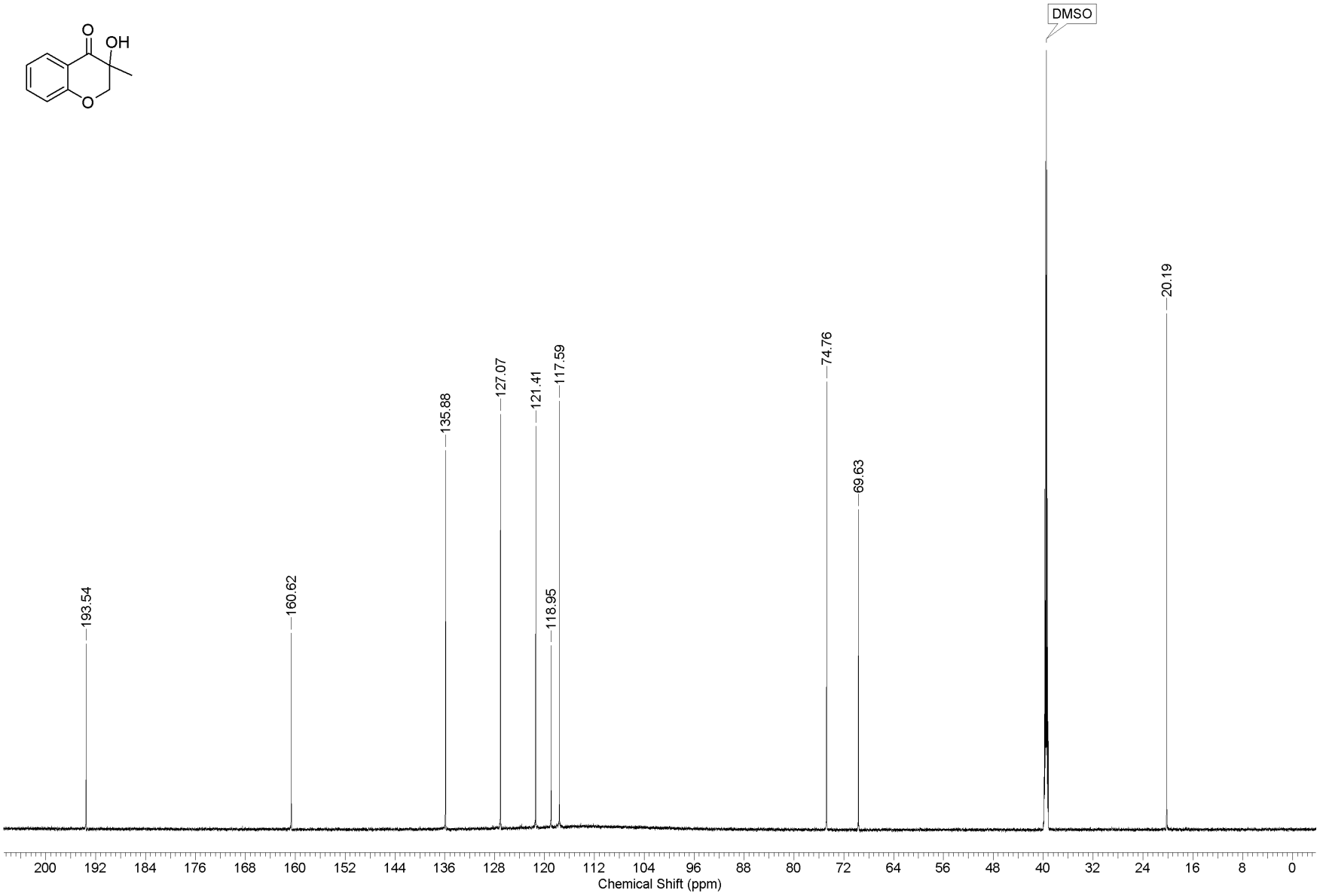

F
O
OH
OH
F
O
F
DMSO
8.10
7.69
7.68
7.68
7.67
7.67
7.66
7.64
7.64
7.63
7.63
7.41
7.40
7.39
7.39
1.90
1.03
0.98
1.02
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
Chemical Shift (ppm)
8.10
Water
7.67
7.67
7.66
7.64
7.63
7.41
7.40
7.39
7.39
1.90
0.98
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


O
OH
OH
F
F
O
F
DMSO
158.89
157.68
149.92
149.92
124.91
124.78
123.68
122.34
121.00
120.12
120.08
118.88
118.85
112.97
112.85
89.15
88.99
88.84
187.48
158.89
157.68
149.92
124.91
124.78
122.34
120.08
118.88
118.85
112.97
112.85
89.15
88.99
88.84
Chemical Shift (ppm)
Chemical Shift (ppm)
Chemical Shift (ppm)
Chemical Shift (ppm)


O
OH
OH
F
F
O
OMe
Water
DMSO
7.97
7.48
7.48
7.47
7.47
7.42
7.42
7.41
7.41
7.28
7.27
7.26
3.88
1.95
1.00
0.99
0.99
Chemical Shift (ppm)
7.97
7.48
7.47
7.42
7.41
7.27
7.26
1.95
1.00
0.99
3.08
Chemical Shift (ppm)


O
OH
OH
F
F
O
OMe
DMSO
148.03
143.19
89.13
88.98
88.82
124.57
123.90
122.56
121.22
119.58
118.49
118.02
56.30
188.37
Chemical Shift (ppm)


O
OH
O
DMSO
Water
1.26
7.78
7.78
7.77
7.77
7.58
7.57
7.57
7.56
7.56
7.10
7.09
7.08
7.08
7.04
7.03
1.00
0.99
1.00
0.98
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
Chemical Shift (ppm)
5.83
4.24
4.22
4.25
4.21
7.78
7.78
7.77
7.77
7.57
7.57
7.56
7.56
7.10
7.09
7.04
7.03
1.00
0.99
0.98
1.01
1.99
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


O
OH
O
DMSO
193.54
160.62
135.88
127.07
121.41
118.95
117.59
74.76
69.63
20.19
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)