Electronic supplementary materials *Mendeleev Commun.*, 2026, **36**, 164–166

Photochemical synthesis of 3,4-dihydro-1-benzoxepine-2,5-diones from 2-formylaryl acrylates

Svetlana A. Krasnova, Alexander Yu. Smirnov, Viktoria A. Ikonnikova, Andrey A. Mikhaylov, Mikhail S. Baranov and Dmitrii S. Ivanov

S1. Reagents and methods.

NMR spectra ^{1}H, ^{13}C, C-H HSQC, C-H HMBC were recorded on a Bruker Avance III 800 and Bruker Fourier 300 instruments. Chemical shifts were reported relative to solvents residue peaks (2.50 ppm for ^{1}H and 39.52 ppm for ^{13}C in DMSO-d_6 and 7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C in $CDCl_3$).

High-resolution mass spectra (HRMS) spectra were recorded on TripleTOF 5600+ system using electrospray ionization (ESI).

Melting points were measured on a SMP 30 apparatus.

Photoinduced processes were performed on Evoluchem™ PhotoRedOx box. 365 nm (LG, HCK1012-01-006, 25 mW/cm^2), 380 nm (LG, HCK1012-01-013, 8 mW/cm^2), 405 nm (LG, HCK1012-01-010, 28 mW/cm^2) and 425 nm (EPILED, HCK1012-01-012, 33 mW/cm^2) light-emitting diode (LED) lamps from Evoluchem™ were used.

Absorption spectrum of 2-formylphenylacrylate **1a** was recorded on a Cary 100 Bio spectrophotometer (Varian, United States) using a 200 μM solution in dry DMSO. Spectrum processing was performed using OriginPro 8.6 software (https://www.originlab.com/).

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 aluminium plates (MERCK).

2-Formylphenylacrylate **1a**,[S1] and 2-formylphenyl-(E)-but-2-unoate **1f**,[S2] were obtained according to previously proposed protocols and their spectral data correspond to those described.

S2. Experiments with radical quenching reagents.

Compound **1a** (15 mg, 0.09 mmol) was dissolved in 3 mL of DMSO-d_6 in a Schlenk vessel. The mixture was degassed under vacuum and filled with argon three times. Next, parts of the solution (0.65 mL) were transferred to three argon-filled NMR tubes and sealed. (2,2,6,6-Tetramethylpiperidin-1-yl)oxidanyl (TEMPO, 6 mg, 0.04 mmol) was added to one tube, butylated hydroxytoluene (BHT, 8 mg, 0.04 mmol) was added to the second, 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. The mixtures were analyzed by ^{1}H NMR.

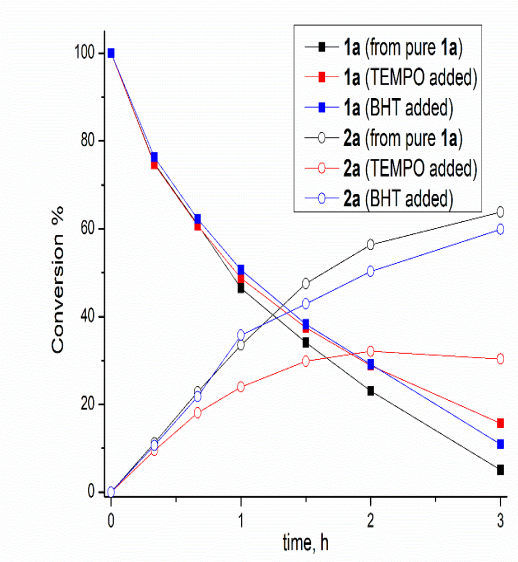
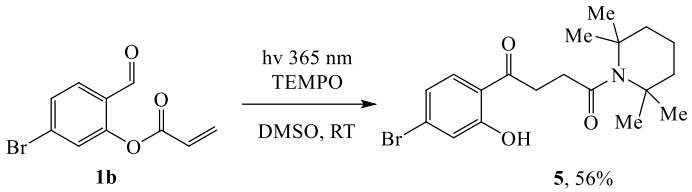


Figure S1. Kinetic study of **1a** phototranformation with BHT and TEMPO.



Compound **1b** (100 mg, 0.39 mmol) was dissolved in 5 mL of DMSO under inert atmosphere and TEMPO (244 mg, 1.56 mmol, 5 eq.) was added. The obtained solution was irradiated with 365 nm LED lamp with stirring for 24 hours. After the reaction completion, the mixture was dissolved in 100 mL of EtOAc, washed with saturated KCl solution (5×50 mL) and dried over Na_2SO_4. All volatiles were removed *in vacuo* and the residue was purified by flash chromatography (eluent hexane–EtOAc 3:1 v/v).

1-(2-Hydroxyphenyl)-4-(2,2,6,6-tetramethylpiperidin-1-yl)butane-1,4-dione **5**: Yield 69 mg (56%), colorless oil. ^{1}H NMR (300 MHz, DMSO-d_6), δ: 11.70 (1H, s, OH), 7.80 (1H, d, J = 8.4 Hz, Ar), 7.22 (1H, d, J = 1.8 Hz, Ar), 7.15 (1H, dd, J = 8.6, 1.8 Hz, Ar), 3.36 – 3.40 (2H, m, CO-CH_2-CH_2), 2.7 (2H, t, J = 6.1 Hz, CO-CH_2-CH_2), 1.35 – 1.55 (6H, m, CH_2-CH_2-CH_2), 1.06 (6H, s, CH_3), 0.95 (6H, s, CH_3).

S3. Optimization of wavelength.

Compound **1a** (20 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, 0.65 mL portions of the solution were transferred to four argon flushed NMR tube and sealed. The mixtures were analyzed by ^{1}H NMR (initial point). The NMR tubes with this solution were irradiated with different LED lamps (365, 380, 405, and 425 nm separately) in Evoluchem™ PhotoRedOx box for an hour. The mixtures were analyzed by ^{1}H NMR.

Table S1. Yield of **2a** at different wavelengths

Wavelength, nm	Yield **2a**, %	Remained **1a**, %
365	33	46
380	20	69
405	0	98
425	0	100

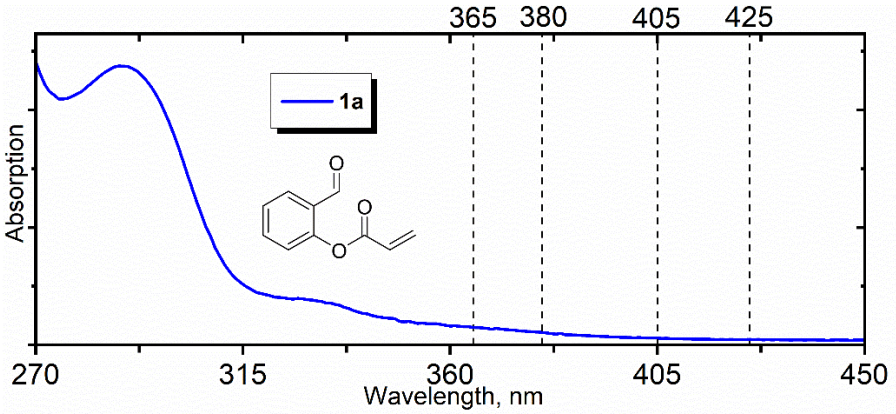
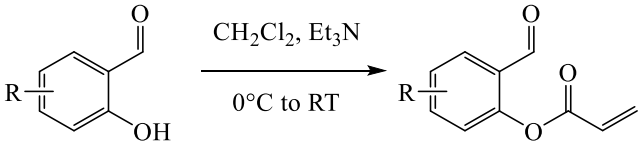


Figure S2. The absorption spectrum of compound **1a**. Irradiation wavelengths are marked with dashed lines.

S4. General synthetic procedure for 2-formylphenyl acrylates (1b-k).[S1]



1b-k

The corresponding 2-hydroxybenzaldehyde (2.5 mmol) was dissolved in freshly distilled CH_2Cl_2 (8 mL), and cooled to 0°C. Triethylamine (0.38 g, 3.75 mmol, 0.52 mL) and acryloyl chloride (0.34 g, 3.75 mmol, 0.31 mL) were added subsequently. The resulted mixture was stirred at room temperature for two hours. Next, the reaction mixtures were diluted with CH_2Cl_2 (100 mL), washed with water (100 mL) and dried over Na_2SO_4. All volatiles were removed *in vacuo* and the residue was purified by flash chromatography (eluent hexane and EtOAc mixtures, 9:1 for compounds **1b-d**, **1f-k**, and 3:1 for compound **1e**).

5-Bromo-2-formylphenyl acrylate **1b**: Yield 592 mg (93%), white solid, m.p. 69-71 °C. ^{1}H NMR (800 MHz, DMSO-d_6) δ: 10.00 (1H, s, C<u>H</u>O), 7.86 (1H, d, J = 8.1 Hz, H-3 Ar), 7.75 (1H, dd, J = 8.2, 1.7 Hz, H-4 Ar), 7.73 (1H, d, J = 1.7 Hz, H-6 Ar), 6.57 (1H, dd, J = 17.3, 1.0 Hz, CH=C<u>H</u>$_2$), 6.44 (1H, dd, J = 17.3, 10.5 Hz, C<u>H</u>=CH$_2$), 6.21 (1H, J = 10.5, 1.0 Hz, CH=C<u>H</u>$_2$). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 189.0 (<u>C</u>HO), 163.7 (<u>C</u>OOAr), 151.0 (Ar), 134.5 (CH=<u>C</u>H$_2$), 132.6 (Ar), 130.0 (Ar), 128.4 (Ar), 127.1 (Ar), 127.0 (Ar), 126.9 (<u>C</u>H=CH$_2$). HRMS (ESI), *m/z*: 308.9737 [M+Na+MeOH]$^+$, (calc. for $C_{11}H_{11}BrNaO_4^+$, *m/z*: 308.9733).

4-Ethyl-2-formylphenyl acrylate **1c**: Yield 475 mg (93%), colorless oil. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 10.02 (1H, s, C<u>H</u>O), 7.77 (1H, d, J = 2.2 Hz, H-3 Ar), 7.62 (1H, dd, J = 8.3, 2.2 Hz, H-5 Ar), 7.27 (1H, J = 8.3 Hz, H-6 Ar), 6.57 (1H, dd, J = 17.2, 1.7 Hz, CH=C<u>H</u>$_2$), 6.46 (1H, dd, J = 17.2, 9.9 Hz, C<u>H</u>=CH$_2$), 6.19 (1H, dd, J = 9.9, 1.7 Hz, CH=C<u>H</u>$_2$), 2.71 (2H, q, J = 7.6 Hz, C<u>H</u>$_2$CH$_3$), 1.22 (3H, t, J = 7.6 Hz, CH$_2$C<u>H</u>$_3$). NMR ^{13}C NMR (75 MHz, DMSO-d_6) δ: 189.7 (<u>C</u>HO), 164.2 (<u>C</u>OOAr), 148.7 (Ar), 142.4 (Ar), 135.0 (Ar), 133.9 (CH=<u>C</u>H$_2$), 130.2 (Ar), 127.6 (Ar), 127.3 (<u>C</u>H=CH$_2$), 123.5 (Ar), 27.3 (<u>C</u>H$_2$CH$_3$), 15.3 (CH$_2$<u>C</u>H$_3$). HRMS (ESI), *m/z*: 219.1019 [M+CH$_3$OH+]$^+$, (calc. for $C_{13}H_{15}O_3^+$, *m/z*: 219.1016).

4-Bromo-2-formyl-6-methoxyphenyl acrylate **1d**: Yield 600 mg (84%), yellow solid, m.p. 85-87°C. ^{1}H NMR (800 MHz, DMSO-d_6) δ: 10.01 (1H, s, C<u>H</u>O), 7.72 (1H, d, J = 2.2 Hz, H-3 Ar), 7.63 (1H, d, J = 2.2 Hz, H-5 Ar), 6.59 (1H, dd, J = 17.3, 1.0 Hz, CH=C<u>H</u>$_2$), 6.47 (1H, dd, J = 17.3, 10.5 Hz, C<u>H</u>=CH$_2$), 6.23 (1H, dd, J = 10.5, 1.0 Hz, CH=C<u>H</u>$_2$), 3.88 (3H, s, C<u>H</u>$_3$). NMR ^{13}C NMR (75 MHz, CDCl$_3$) δ: 187.1 (<u>C</u>HO), 163.5 (<u>C</u>OOAr), 152.7 (Ar), 141.3 (Ar), 134.2 (CH=<u>C</u>H$_2$), 130.2 (Ar), 126.6 (<u>C</u>H=CH$_2$), 123.1 (Ar), 121.0 (Ar), 120.2 (Ar), 56.8 (O<u>C</u>H$_3$). HRMS (ESI), *m/z*: 284.9759 [M+H]$^+$, (calc. for $C_{11}H_{10}BrO_4^+$, *m/z*: 284.9757).

2-Formyl-4-(pyrimidin-2-yl)phenyl acrylate **1e**: Yield 407 mg (64%), yellow solid, m.p. 129-131°C. ^{1}H NMR (800 MHz, DMSO-d_6) δ: 10.17 (1H, s, C<u>H</u>O), 8.98 (2H, d, J = 4.8 Hz, HetAr), 8.95 (1H, d, J = 2.0 Hz, H-3 Ar), 8.74 (1H, dd, J = 8.4, 2.0 Hz, H-5 Ar), 7.56 (1H, d, J = 8.4 Hz, H-6 Ar), 7.54 (1H, t, J

= 4.8 Hz, HetAr), 6.63 (1H, d, *J* = 17.3 Hz, CH=C$\underline{H}_2$), 6.51 (1H, dd, *J* = 17.3, 10.5 Hz, C$\underline{H}$=CH$_2$), 6.25 (1H, d, *J* = 10.5 Hz, CH=C$\underline{H}_2$). NMR ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 188.6 (C$\underline{H}$O), 164.1 (HetAr), 163.0 (C$\underline{O}$OAr), 157.5 (2C, HetAr), 153.3 (Ar), 136.3 (Ar), 134.8 (CH=C$\underline{H}_2$), 134.0 (Ar), 131.4 (Ar), 128.3 (Ar), 127.3 (C$\underline{H}$=CH$_2$), 123.9 (Ar), 119.8 (Ar). HRMS (ESI), *m/z*: 255.0767 $[M+H]^+$, (calc. for $C_{14}H_{11}N_2O_3^+$, *m/z*: 255.0764).

Methyl 4-(acryloyloxy)-3-formylbenzoate **1g**: Yield 410 mg (70%), white solid, m.p. 110-112°C. ^{1}H NMR (300 MHz, DMSO-*d*$_6$) *δ*: 10.11 (1H, s, C$\underline{H}$O), 8.49 (2H, d, *J* = 2.2 Hz, H-2 Ar), 8.30 (1H, dd, *J* = 8.4, 2.2 Hz, H-6 Ar), 7.56 (1H, d, *J* = 8.4 Hz, H-5 Ar), 6.62 (1H, dd, *J* = 17.2, 1.4 Hz, CH=C$\underline{H}_2$), 6.49 (1H, dd, *J* = 17.2, 10.1 Hz, C$\underline{H}$=CH$_2$), 6.25 (1H, dd, *J* = 10.1, 1.4 Hz, CH=C$\underline{H}_2$), 3.91 (3H, s, COOC$\underline{H}_3$). NMR ^{13}C NMR (75 MHz, DMSO-*d*$_6$) *δ*: 189.3 (C$\underline{H}$O), 164.8 (C$\underline{O}$OAr), 163.5 (C$\underline{O}$OCH$_3$), 153.8 (Ar), 135.8 (Ar), 134.7 (CH=C$\underline{H}_2$), 132.2 (Ar), 128.0 (2C, Ar), 127.0 (C$\underline{H}$=CH$_2$), 124.6 (Ar), 52.6 (COO$\underline{C}$H$_3$).

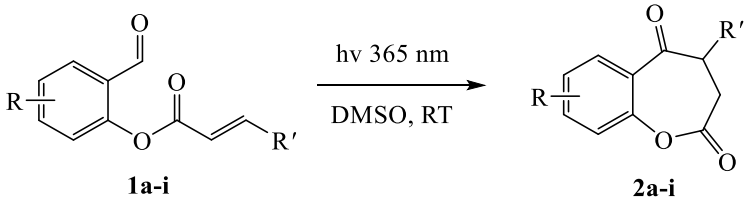
2-Formyl-4-iodophenyl acrylate **1h**: Yield 468 mg (62%), light yellow solid, m.p. 70-72°C. ^{1}H NMR (300 MHz, DMSO-*d*$_6$) *δ*: 9.96 (1H, s, C$\underline{H}$O), 8.23 (1H, d, *J* = 2.2 Hz, H-3 Ar), 8.10 (1H, dd, *J* = 8.5, 2.2 Hz, H-5 Ar), 7.21 (1H, d, *J* = 8.5 Hz, H-6 Ar), 6.58 (1H, dd, *J* = 17.2, 1.5 Hz, CH=C$\underline{H}_2$), 6.45 (1H, dd, *J* = 17.2, 10.1 Hz, C$\underline{H}$=CH$_2$), 6.21 (1H, dd, *J* = 10.1, 1.5 Hz, CH=C$\underline{H}_2$). NMR ^{13}C NMR (75 MHz, DMSO-*d*$_6$) *δ*: 188.8 (C$\underline{H}$O), 163.7 (C$\underline{O}$OAr), 150.2 (Ar), 143.8 (Ar), 139.7 (Ar), 134.4 (CH=C$\underline{H}_2$), 129.6 (Ar), 127.1 (C$\underline{H}$=CH$_2$), 126.1 (Ar), 91.5 (Ar).

1-Formylnaphthalen-2-yl acrylate **1i**: Yield 407 mg (72%), light yellow solid, m.p. 60-62°C. ^{1}H NMR (300 MHz, DMSO-*d*$_6$) *δ*: 10.62 (1H, s, C$\underline{H}$O), 9.04 (1H, d, *J* = 8.6 Hz, H-9 Ar), 8.36 (1H, d, *J* = 9.0 Hz, H-4 Ar), 8.10 (1H, d, *J* = 8.3 Hz, H-6 Ar), 7.72 – 7.80 (1H, m, H-7 Ar), 7.62 – 7.70 (1H, m, H-8 Ar), 7.53 (1H, d, *J* = 8.9 Hz, H-3 Ar), 6.66 (1H, dd, *J* = 17.2, 1.1 Hz, CH=C$\underline{H}_2$), 6.54 (1H, dd, *J* = 17.2, 9.9 Hz, C$\underline{H}$=CH$_2$), 6.27 (1H, dd, *J* = 10.0, 1.1 Hz, CH=C$\underline{H}_2$). NMR ^{13}C NMR (75 MHz, DMSO-*d*$_6$) *δ*: 190.7 (C$\underline{H}$O), 164.2 (C$\underline{O}$OAr), 153.7 (Ar), 136.7 (Ar), 134.7 (CH=C$\underline{H}_2$), 131.4 (Ar), 130.3 (Ar), 129.6 (Ar), 128.8 (Ar), 127.1 (C$\underline{H}$=CH$_2$), 126.7 (Ar), 124.3 (Ar), 122.2 (Ar), 121.0 (Ar).

2-Formyl-4-(thiophen-2-yl)phenyl acrylate **1j**: Yield 387 mg (60%), light yellow solid, m.p. 82-84°C. ^{1}H NMR (300 MHz, DMSO-*d*$_6$) *δ*: 10.08 (1H, s, C$\underline{H}$O), 8.17 (1H, d, *J* = 2.4 Hz, H-3 Ar), 8.05 (1H, dd, *J* = 8.5, 2.4 Hz, H-5 Ar), 7.62 – 7.68 (2H, m, HetAr), 7.43 (1H, d, *J* = 8.4 Hz, H-6 Ar), 7.17 – 7.22 (1H, m, HetAr), 6.60 (1H, dd, *J* = 17.2, 1.5 Hz, CH=C$\underline{H}_2$), 6.48 (1H, dd, *J* = 17.3, 10.0 Hz, C$\underline{H}$=CH$_2$), 6.22 (1H, dd, *J* = 10.1, 1.4 Hz, CH=C$\underline{H}_2$). ^{13}C NMR (75 MHz, DMSO-*d*$_6$) *δ*: 189.7 (C$\underline{H}$O), 164.0 (C$\underline{O}$OAr), 149.5 (Ar), 141.1 (HetAr), 134.2 (CH=C$\underline{H}_2$), 132.4 (Ar), 132.0 (Ar), 128.8 (Ar), 128.3 (Ar), 127.9 (C$\underline{H}$=CH$_2$), 127.2 (HetAr), 126.8 (HetAr), 125.0 (Ar), 124.6 (HetAr).

5-(Diethylamino)-2-formylphenyl acrylate **1k**: Yield 550 mg (89%), pink oil. ^{1}H NMR (300 MHz, DMSO-*d*$_6$) *δ*: 9.62 (1H, s, C$\underline{H}$O), 7.64 (1H, d, *J* = 8.9 Hz, H-3 Ar), 6.68 (1H, dd, *J* = 8.9, 2.3 Hz, H-4 Ar), 6.35 – 6.57 (3H, m, C$\underline{H}$=CH$_2$, CH=C$\underline{H}_2$ and H-6 Ar), 6.15 (1H, dd, *J* = 9.8, 1.7 Hz, CH=C$\underline{H}_2$), 3.43 (4H, q, *J* = 7.0 Hz, C$\underline{H}_2$CH$_3$), 1.11 (6H, t, *J* = 7.0 Hz, CH$_2$C$\underline{H}_3$). ^{13}C NMR (75 MHz, DMSO-*d*$_6$) *δ*: 186.0 (C$\underline{H}$O), 164.0 (C$\underline{O}$OAr), 153.1 (Ar), 152.8 (Ar), 133.5 (CH=C$\underline{H}_2$), 133.4 (Ar), 127.7 (C$\underline{H}$=CH$_2$), 115.5 (Ar), 108.6 (Ar), 104.4 (Ar), 44.1 (2C, C$\underline{H}_2$CH$_3$), 12.3 (2C, CH$_2$C$\underline{H}_3$).

S5. General synthetic procedure for 3,4-dihydro-1-benzoxepine-2,5-diones (2a-i).



1a-i **2a-i**

The corresponding aldehyde **1a-i** (0.7 mmol) was dissolved in freshly distilled DMSO (8 mL) under inert atmosphere. The obtained solutions were irradiated with 365 nm LED lamp with stirring for 24 hours. The reaction progress was monitored by TLC (hexane and EtOAc mixtures, 3:1 for compounds **2a-d**, **2f-i** and 1:1 for compound **2e**). After the reaction completion, the mixtures were dissolved in 100 mL of EtOAc, washed with saturated KCl solution (5×50 mL) and dried over Na_2SO_4. All volatiles were removed *in vacuo* and the residue was purified by flash chromatography (abovementioned

eluents). For compound **2c** an acid **3** was also isolated. For compound **2d** a minor admixture of compound **4** was revealed.

3,4-Dihydro-1-benzoxepine-2,5-dione **2a**: Yield 71 mg (58%), yellow solid, m.p. 75-77°C. ^{1}H NMR (300 MHz, DMSO-*d*$_6$) *δ*: 7.67 – 7.75 (2H, m, H-Ar), 7.42 (1H, td, *J* = 7.6, 1.1 Hz, H-Ar), 7.24 – 7.31 (1H, m, H-Ar), 3.00 – 3.09 (2H, m, C$\underline{H_2}$C(O)Ar), 2.87 – 2.97 (2H, m, C$\underline{H_2}$COO). ^{13}C NMR (75 MHz, DMSO-*d*$_6$) *δ*: 198.9 (CH$_2\underline{C}$(O)Ar), 169.9 (CH$_2\underline{C}$OO), 151.1 (Ar), 134.9 (Ar), 130.0 (Ar), 127.8 (Ar), 126.0 (Ar), 121.5 (Ar), 37.9 ($\underline{C}$H$_2$C(O)Ar), 27.9 ($\underline{C}$H$_2$COO). ^{13}C–^{1}H HSQC (the most important cross-peaks): H(3.00 – 3.09)/C(37.9), H(2.87 – 2.97)/C(27.9). ^{13}C–^{1}H HMBC (the most important cross-peaks): H(3.00 – 3.09)/C(198.9), H(2.87 – 2.97)/C(198.9). HRMS (ESI), *m/z*: 177.0546 [M+H]$^+$, (calc. for $C_{10}H_9O_3^+$, *m/z*: 177.0546).

8-Bromo-3,4-dihydro-1-benzoxepine-2,5-dione **2b**: Yield 98 mg (55%), yellow solid, m.p. 101-103°C. ^{1}H NMR (800 MHz, DMSO-*d*$_6$) *δ*: 7.67 (1H, d, *J* = 8.3 Hz, H-Ar), 7.65 (1H, dd, *J* = 8.3, 1.7 Hz, H-Ar), 7.58 (1H, d, *J* = 1.7 Hz, H-Ar), 3.05 – 3.07 (2H, m, C$\underline{H_2}$C(O)Ar), 2.95 – 2.98 (2H, m, C$\underline{H_2}$COO). ^{13}C NMR (75 MHz, DMSO-*d*$_6$) *δ*: 198.0 (CH$_2\underline{C}$(O)Ar), 169.3 (CH$_2\underline{C}$OO), 151.5 (Ar), 131.7 (Ar), 129.0 (Ar), 127.5 (Ar), 126.9 (Ar), 124.6 (Ar), 37.7 ($\underline{C}$H$_2$C(O)Ar), 27.6 ($\underline{C}$H$_2$COO). HRMS (ESI), *m/z*: 254.9651 [M+H]$^+$, (calc. for $C_{10}H_8BrO_3^+$, *m/z*: 254.9651).

7-Ethyl-3,4-dihydro-1-benzoxepine-2,5-dione **2c**: Yield 70 mg (49%), white solid, m.p. 41-43°C. ^{1}H NMR (800 MHz, DMSO-*d*$_6$) *δ*: 7.54 – 7.58 (2H, m, H-Ar), 7.21 (1H, d, *J* = 8.2 Hz, H-Ar), 3.03 – 3.06 (2H, m, C$\underline{H_2}$C(O)Ar), 2.91 – 2.95 (2H, m, C$\underline{H_2}$COO), 2.70 (2H, q, *J* = 7.6 Hz, C$\underline{H_2}$CH$_3$), 1.23 (3H, t, *J* = 7.6 Hz, CH$_2$C$\underline{H_3}$). ^{13}C NMR (75 MHz, DMSO-*d*$_6$) *δ*: 199.0 (CH$_2\underline{C}$(O)Ar), 170.1 (CH$_2\underline{C}$OO), 149.3 (Ar), 141.5 (Ar), 134.3 (Ar), 128.6 (Ar), 127.5 (Ar), 121.5 (Ar), 37.9 ($\underline{C}$H$_2$C(O)Ar), 27.9 ($\underline{C}$H$_2$COO), 27.1 ($\underline{C}$H$_2$CH$_3$), 15.3 (CH$_2\underline{C}$H$_3$). HRMS (ESI), *m/z*: 205.0859 [M+H]$^+$, (calc. for $C_{12}H_{13}O_3^+$, *m/z*: 205.0859).

4-(5-Ethyl-2-hydroxyphenyl)-4-oxobutanoic acid **3**: Yield 12 mg (8%), yellow solid, m.p. 132-134°C. ^{1}H NMR (300 MHz, CDCl$_3$) *δ*: 11.88 (1H, s, COO$\underline{H}$), 7.58 (1H, d, *J* = 2.0 Hz, H-6 Ar), 7.34 (1H, dd, *J* = 8.5, 2.1 Hz, H-4 Ar), 6.93 (1H, d, *J* = 8.5 Hz, H-3 Ar), 3.39 (2H, t, *J* = 6.5 Hz, C$\underline{H_2}$C(O)Ar), 2.83 (2H, t, *J* = 6.5 Hz, C$\underline{H_2}$COOH), 2.62 (2H, q, *J* = 7.5 Hz, C$\underline{H_2}$CH$_3$), 1.27 (3H, t, *J* = 7.6 Hz, CH$_2$C$\underline{H_3}$). ^{13}C NMR (201 MHz, CDCl$_3$) *δ*: 203.7 (CH$_2\underline{C}$(O)Ar), 178.1 ($\underline{C}$OOH), 160.5 (Ar), 136.6 (Ar), 134.9 (Ar), 128.4 (Ar), 118.9 (Ar), 118.5 (Ar), 33.0 ($\underline{C}$H$_2$C(O)Ar), 28.1 ($\underline{C}$H$_2$COOH), 27.8 ($\underline{C}$H$_2$CH$_3$), 15.9 (CH$_2\underline{C}$H$_3$). HRMS (ESI), *m/z*: 245.0787 [M+Na]$^+$, (calc. for $C_{12}H_{14}NaO_4^+$, *m/z*: 245.0784).

7-Bromo-9-methoxy-3,4-dihydro-1-benzoxepine-2,5-dione **2d**: Yield 50 mg (25%), yellow solid, m.p. 178-180°C. ^{1}H NMR (800 MHz, DMSO-*d*$_6$) *δ*: 7.60 (1H, d, *J* = 2.3 Hz, H-Ar), 7.29 (1H, d, *J* = 2.3 Hz, H-Ar), 3.92 (3H, s, OC$\underline{H_3}$), 3.06 (2H, dd, *J* = 7.6, 5.0 Hz, C$\underline{H_2}$C(O)Ar), 2.95 (2H, dd, *J* = 7.3, 5.3 Hz, C$\underline{H_2}$COO). ^{13}C NMR (75 MHz, DMSO-*d*$_6$) *δ*: 198.1 (CH$_2\underline{C}$(O)Ar), 169.4 (CH$_2\underline{C}$OO), 151.2 (Ar), 139.8 (Ar), 130.2 (Ar), 122.3 (Ar), 119.8 (Ar), 118.0 (Ar), 56.8 (O$\underline{C}$H$_3$), 38.1 ($\underline{C}$H$_2$C(O)Ar), 27.6 ($\underline{C}$H$_2$COO). HRMS (ESI), *m/z*: 284.9757 [M+H]$^+$, (calc. for $C_{11}H_{10}BrO_4^+$, *m/z*: 284.9757).

5-Bromo-2-hydroxy-7-methoxy-2-vinylbenzofuran-3(2H)-one **4**: detected as a minor impurity in product **2d**. ^{1}H NMR (800 MHz, DMSO-*d*$_6$) *δ*: 7.55 (1H, d, *J* = 1.7 Hz, H-Ar), 7.38 (1H, d, *J* = 1.8 Hz, H-Ar), 5.92 (1H, dd, *J* = 17.2, 10.6 Hz, C$\underline{H}$=CH$_2$), 5.55 (1H, dd, *J* = 17.2, 0.9 Hz, CH=C$\underline{H_2}$), 5.42 (1H, dd, *J* = 10.6, 0.9 Hz, CH=C$\underline{H_2}$), 3.95 (3H, s, OC$\underline{H_3}$).

7-(Pyrimidin-2-yl)-3,4-dihydro-1-benzoxepine-2,5-dione **2e**: Yield 132 mg (74%), white solid, m.p. 217-219°C. ^{1}H NMR (300 MHz, DMSO-*d*$_6$) *δ*: 8.97 (2H, d, *J* = 4.9 Hz, HetAr), 8.78 (1H, d, *J* = 2.3 Hz, H-6 Ar), 8.64 (1H, dd, *J* = 8.5, 2.3 Hz, H-4 Ar), 7.52 (1H, t, *J* = 4.9 Hz, HetAr), 7.43 (1H, d, *J* = 8.5 Hz, H-3 Ar), 3.07 – 3.14 (2H, m, C$\underline{H_2}$C(O)Ar), 2.96 – 3.04 (2H, m, C$\underline{H_2}$COO). ^{13}C NMR (75 MHz, DMSO-*d*$_6$) *δ*: 198.5 (CH$_2\underline{C}$(O)Ar), 169.5 (CH$_2\underline{C}$OO), 161.6 (Ar), 157.9 (2C, HetAr), 152.7 (Ar), 134.6 (Ar), 133.4 (Ar), 129.7 (Ar), 127.9 (HetAr), 122.4 (Ar), 120.3 (Ar), 37.7 ($\underline{C}$H$_2$C(O)Ar), 27.8 ($\underline{C}$H$_2$COO). HRMS (ESI), *m/z*: 255.0767 [M+H]$^+$, (calc. for $C_{14}H_{11}N_2O_3^+$, *m/z*: 255.0764).

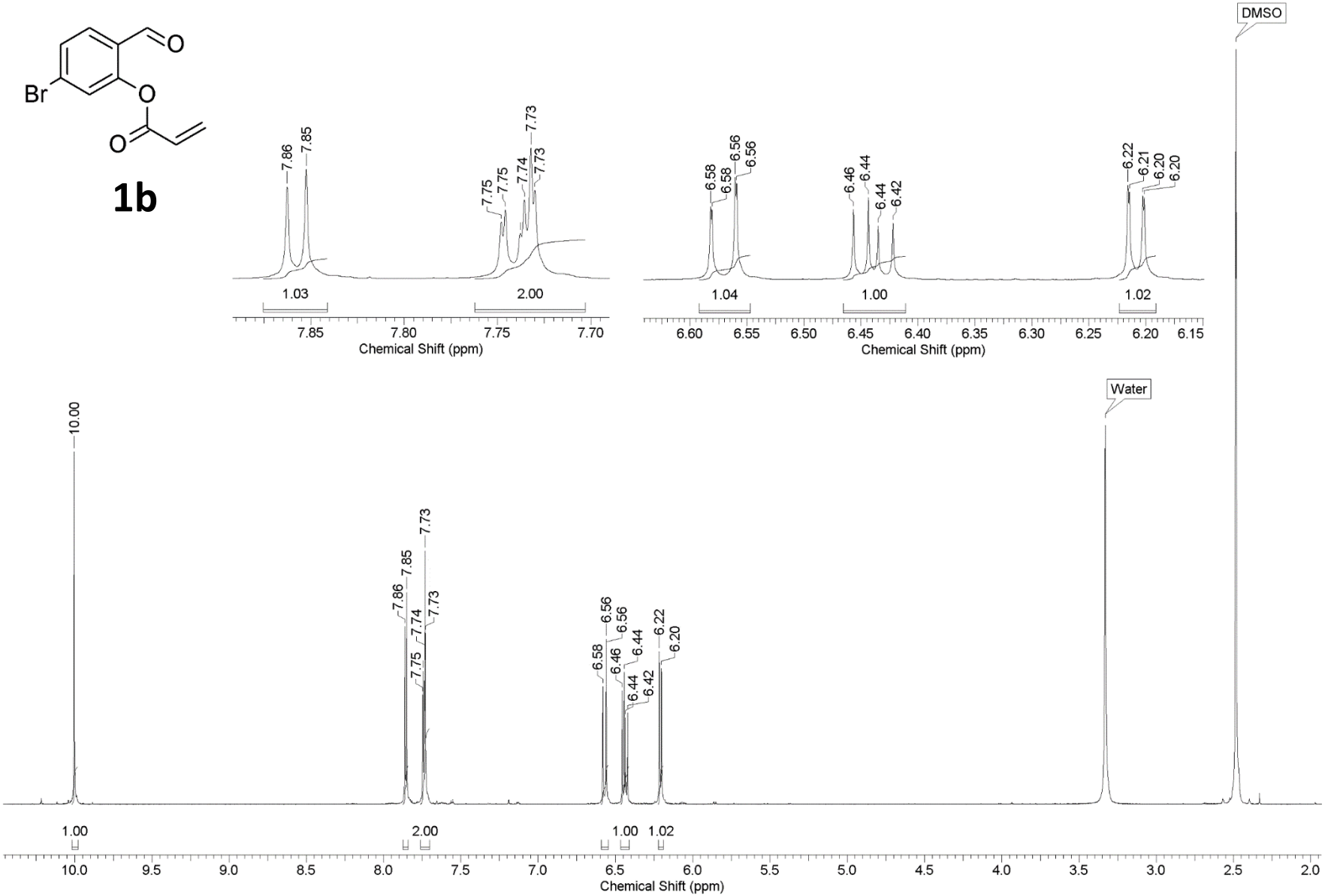
4-Methyl-3,4-dihydro-1-benzoxepine-2,5-dione **2f**: Yield 121 mg (91%), yellow oil. ^{1}H NMR (800 MHz, DMSO-*d*$_6$) *δ*: 7.66 – 7.74 (2H, m, H-Ar), 7.41 (1H, td, *J* = 7.5, 1.1 Hz, H-Ar), 7.24 – 7.31 (1H, m, H-Ar), 2.80 – 3.19 (3H, m, C$\underline{H}$(Me)C$\underline{H_2}$COO), 1.25 (3H, d, *J* = 7.3 Hz, C$\underline{H_3}$). ^{13}C NMR (75 MHz, DMSO-*d*$_6$) *δ*: 202.2 (CH(Me)$\underline{C}$(O)Ar), 168.8 (CH$_2\underline{C}$OO), 150.7 (Ar), 134.7 (Ar), 130.0 (Ar), 128.1 (Ar), 126.0 (Ar), 121.2 (Ar), 42.5 ($\underline{C}$H(Me)), 34.8 (CH(Me)$\underline{C}$H$_2$COO), 16.4 ($\underline{C}$H$_3$). HRMS (ESI), *m/z*: 191.0703 [M+H]$^+$, (calc. for $C_{11}H_{11}O_3^+$, *m/z*: 191.0703).

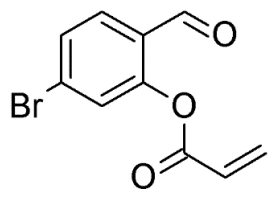
Methyl 2,5-dioxo-2,3,4,5-tetrahydro-1-benzoxepine-7-carboxylate **2g**: Yield 105 mg (64%), white solid, m.p. >200°C (with decomposition). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 8.27 (1H, d, J = 2.1 Hz, H-Ar), 8.19 (1H, dd, J = 8.5, 2.2 Hz, H-Ar), 7.39 (1H, d, J = 8.4 Hz, H-Ar), 3.89 (3H, s, COOC$\underline{H}_3$), 3.03 – 3.11 (2H, m, C$\underline{H}_2$C(O)Ar), 2.92 – 3.00 (2H, m, C$\underline{H}_2$COO). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 198.0 (CH$_2\underline{C}$(O)Ar), 169.1 ($\underline{C}$OOCH$_3$), 164.8 (CH$_2\underline{C}$OO), 154.1 (Ar), 135.0 (Ar), 131.5 (Ar), 127.8 (Ar), 127.0 (Ar), 122.6 (Ar), 52.5 (COO$\underline{C}$H$_3$), 37.6 ($\underline{C}$H$_2$C(O)Ar), 27.7 ($\underline{C}$H$_2$COO).
7-Iodo-3,4-dihydro-1-benzoxepine-2,5-dione **2h**: detected as an inseparable mixture with product **2a** (1:1) in ^{1}H NMR. Yield 49 mg (23%). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.99 (1H, dd, J = 8.5, 2.2 Hz, H-Ar), 7.91 (1H, d, J = 2.2 Hz, H-Ar), 7.07 (1H, d, J = 8.4 Hz, H-Ar), 2.98 – 3.07 (2H, m, C$\underline{H}_2$C(O)Ar), 2.87 – 2.97 (2H, m, C$\underline{H}_2$COO).
2,3-Dihydronaphtho[2,1-b]oxepine-1,4-dione **2i**: Yield 86 mg (54%), white solid, m.p. >200°C (with decomposition). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 8.20 (1H, d, J = 8.9 Hz, H-Ar), 7.97 – 8.07 (2H, m, H-Ar), 7.55 – 7.69 (2H, m, H-Ar), 7.40 (1H, d, J = 8.9 Hz, H-Ar), 3.24 (2H, t, J = 6.5 Hz, C$\underline{H}_2$C(O)Ar), 2.96 (2H, t, J = 6.6 Hz, C$\underline{H}_2$COO). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 202.5 (CH$_2\underline{C}$(O)Ar), 169.9 (CH$_2\underline{C}$OO), 149.4 (Ar), 133.7 (Ar), 131.3 (Ar), 129.7 (Ar), 128.3 (2C, Ar), 126.4 (Ar), 125.2 (Ar), 124.5 (Ar), 120.3 (Ar), 41.6 ($\underline{C}$H$_2$C(O)Ar), 28.3 ($\underline{C}$H$_2$COO).

S6. Methodology for NMR monitoring of aldehydes (1a-k) photochemical transformations.
A corresponding compound **1a-k** (30 mkmol) was dissolved in DMSO-d_6 (0.7 mL) under inert atmosphere in an NMR tube. The obtained solutions were irradiated with 365 nm LED lamp for five hours. NMR spectra were recorded before the irradiation and every hour during the process. NMR spectra for substrate **1d** are given as an example in the part S8.

S7. References.
S1. M. L. N. Rao, B. S. Ramakrishna and S. Nand, *Org. Biomol. Chem.*, 2019, **17**, 9275; https://doi.org/10.1039/C9OB01972C.
S2. R. Kaguchi, A. Katsuyama, T. Sato, S. Takahashi, M. Horiuchi, S. I. Yokota and S. Ichikawa, *J. Am. Chem. Soc.*, 2023, **145**, 3665; https://doi.org/10.1021/jacs.2c12971.

S8. NMR and HRMS spectra images.

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O
O

1b

DMSO
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128.41
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126.98
126.92
135.0 134.5 134.0 133.5 133.0 132.5 132.0 131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0
Chemical Shift (ppm)
189.01
163.66
150.96
134.47
132.61
129.99
127.11
126.98
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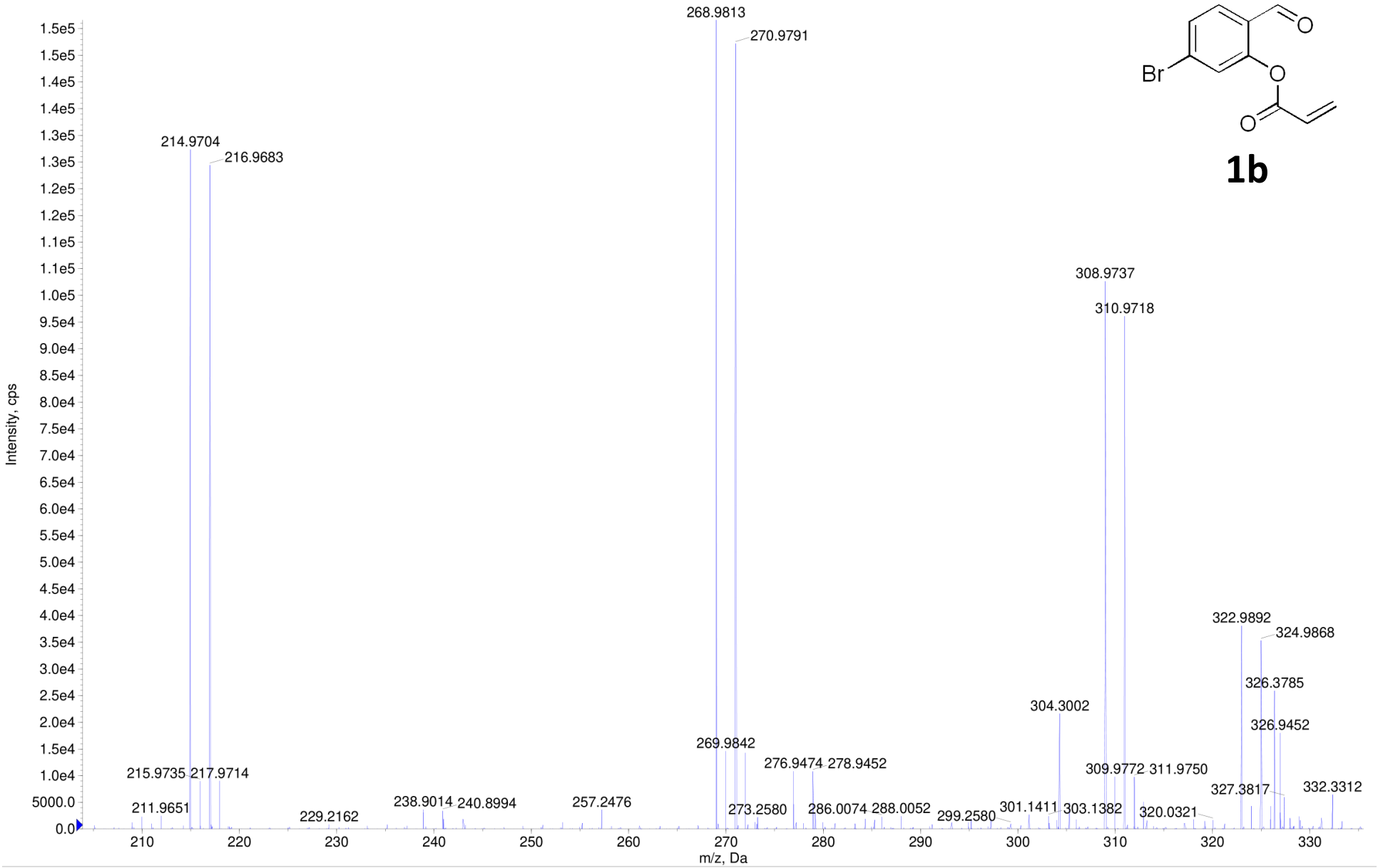
Chemical Shift (ppm)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269.9842
276.9474
278.9452
309.9772
311.9750
215.9735
217.9714
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332.3312
211.9651
229.2162
238.9014
240.8994
257.2476
273.2580
286.0074
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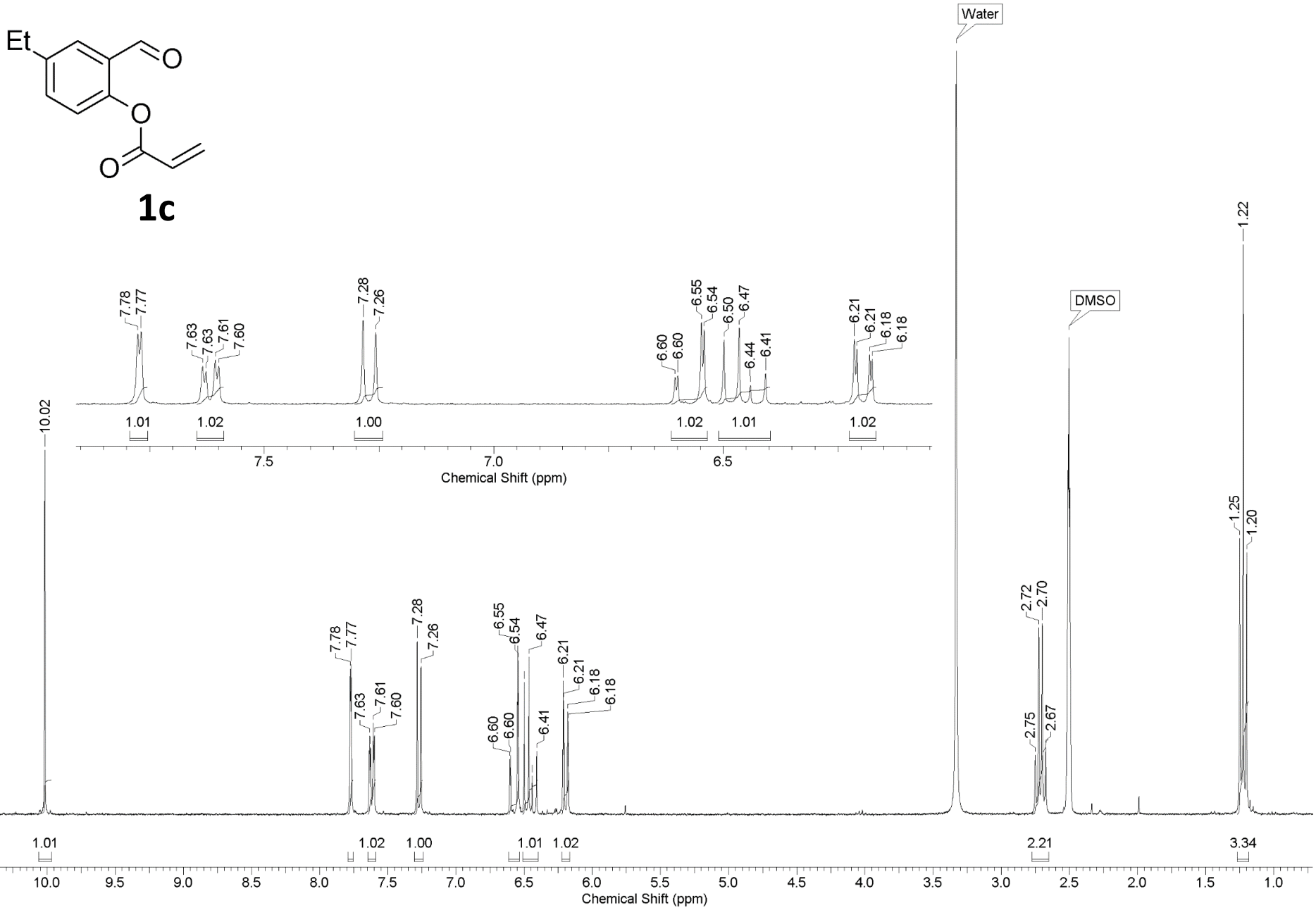
Intensity, cps
m/z, Da
Br
O
O
O
1b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O
O
1c
Water
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6.55
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6.47
6.44
6.41
6.21
6.21
6.18
6.18
2.72
2.70
2.75
2.67
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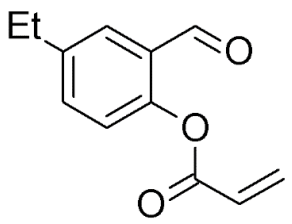
1.01
1.02
1.00
1.02
1.01
1.02
2.21
3.34
Chemical Shift (ppm)


Et
O
O
O

1c

DMSO
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127.29
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136
135
134
133
132
131
130
129
128
127
126
125
124
123
122
Chemical Shift (ppm)
189.71
164.16
148.67
142.41
135.02
133.94
130.16
127.59
127.29
123.53
27.26
15.28
192
184
176
168
160
152
144
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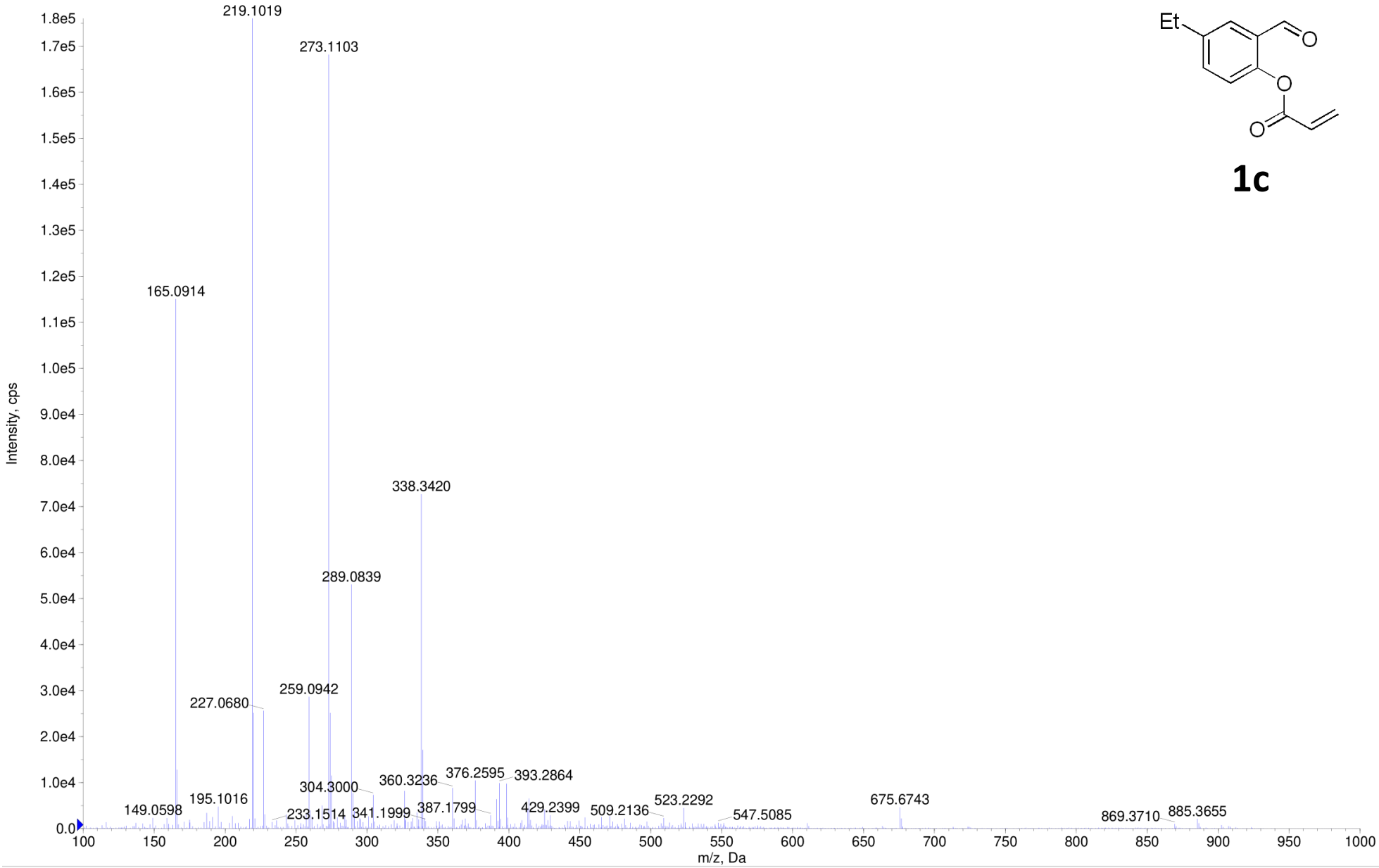
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)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509.2136
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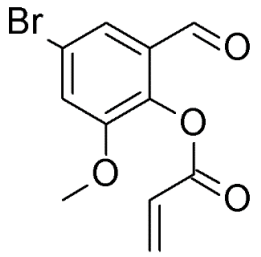
Intensity, cps
m/z, Da
Et
O
O
O

1c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O
O
O

1d

Water
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6.58
6.49
6.48
6.47
6.45
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6.24
6.23
6.22
3.88
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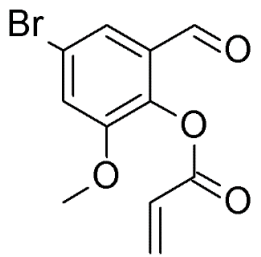
1.05
3.05
Chemical Shift (ppm)
Chemical Shift (ppm)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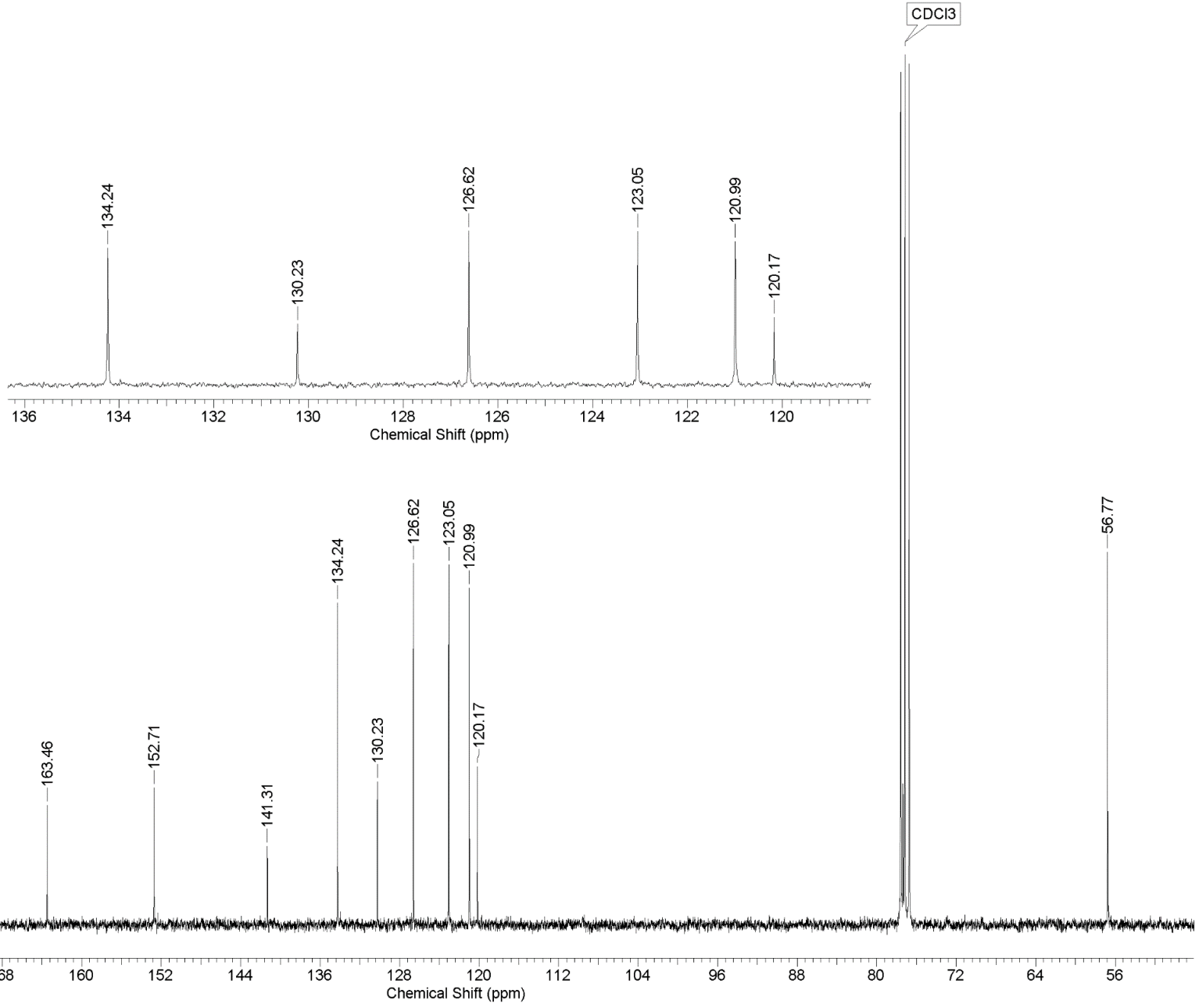
O
O
O
O

1d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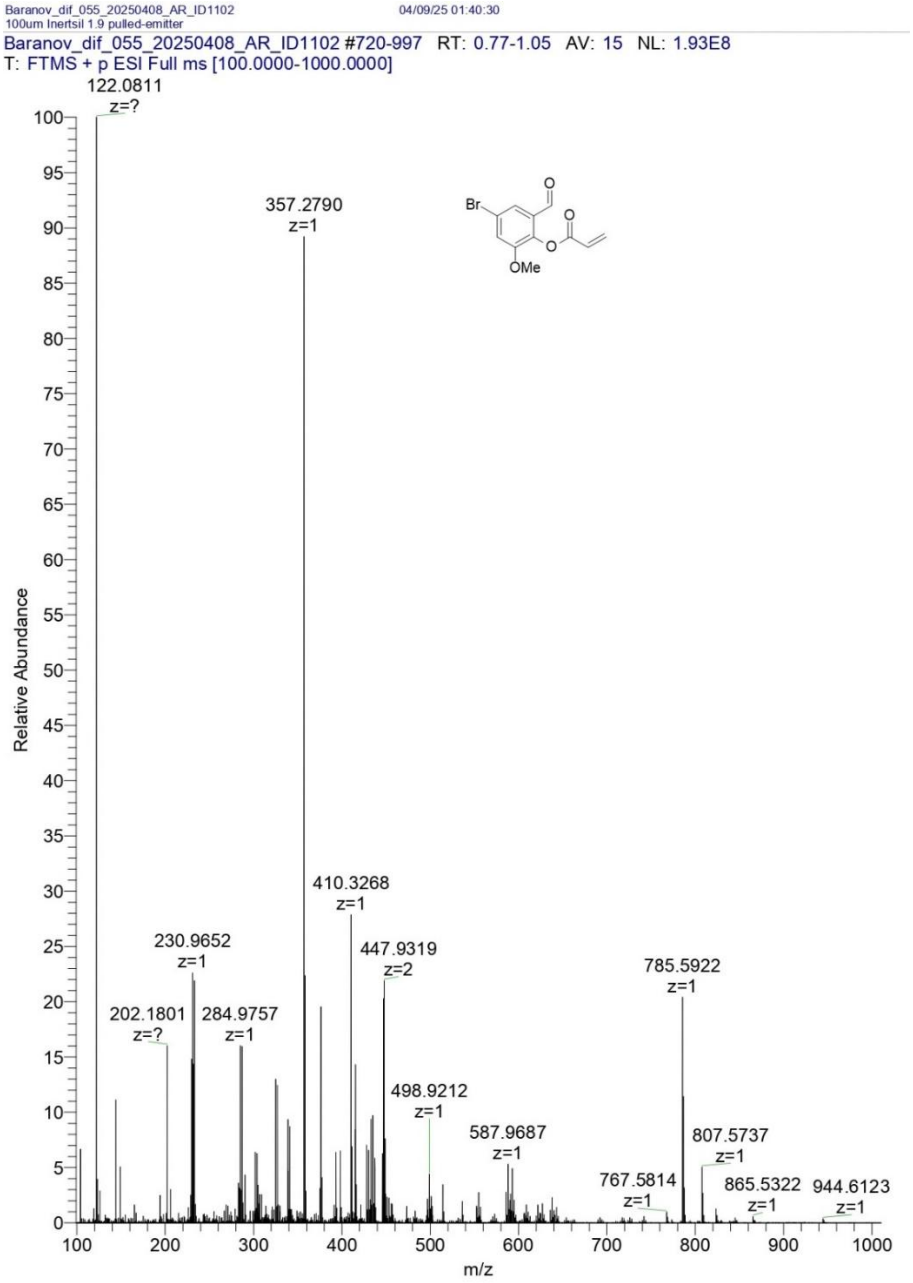
Chemical Shift (ppm)

1d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O
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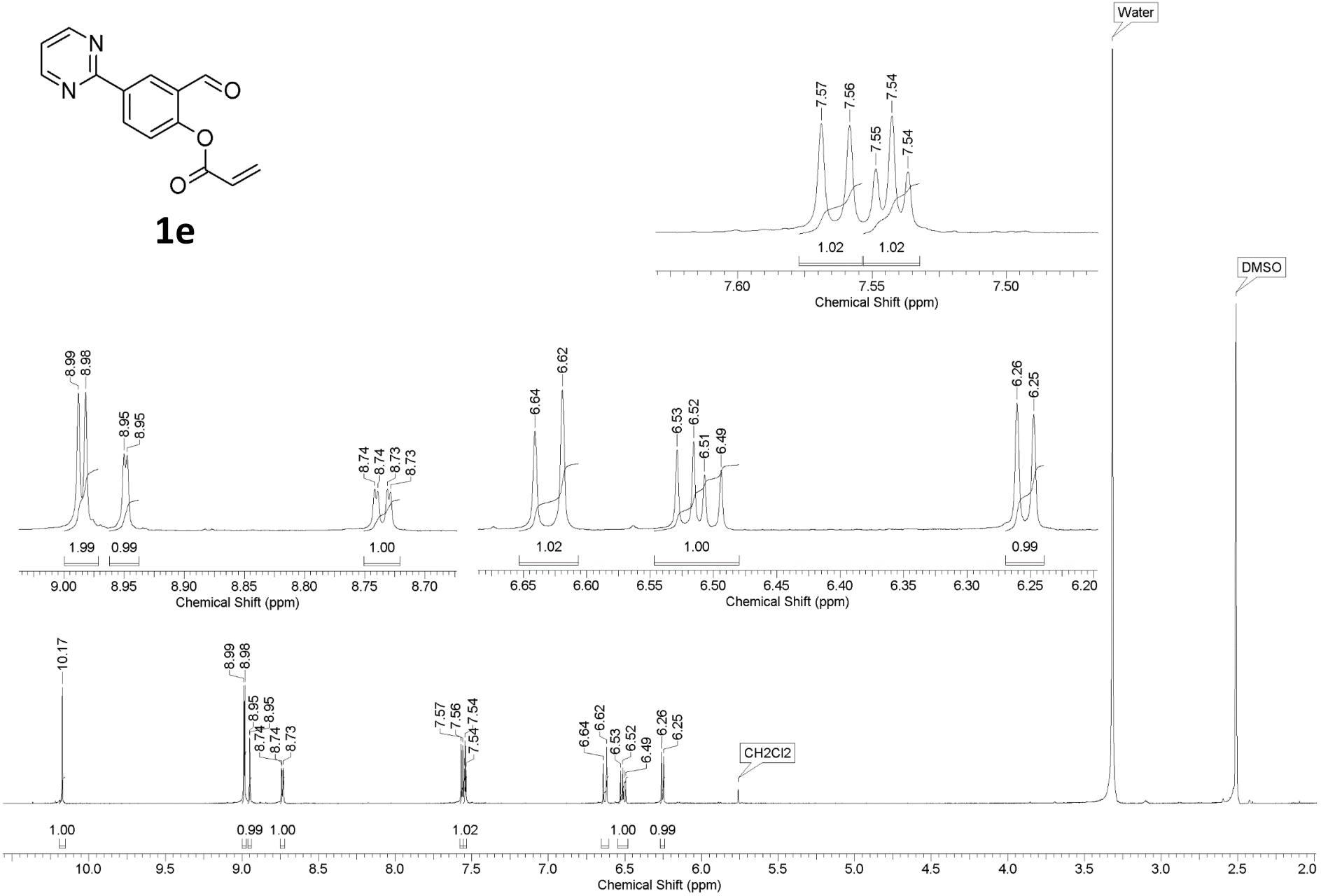
OMe
Relative Abundance
m/z


1e
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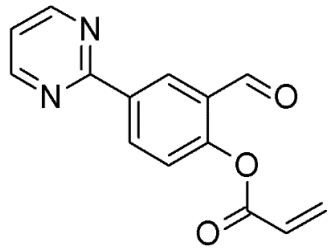
DMSO
CH2Cl2
Chemical Shift (ppm)



1e

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133.97
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128.34
127.25
123.86
119.80
Chemical Shift (ppm)
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134.80
133.97
131.41
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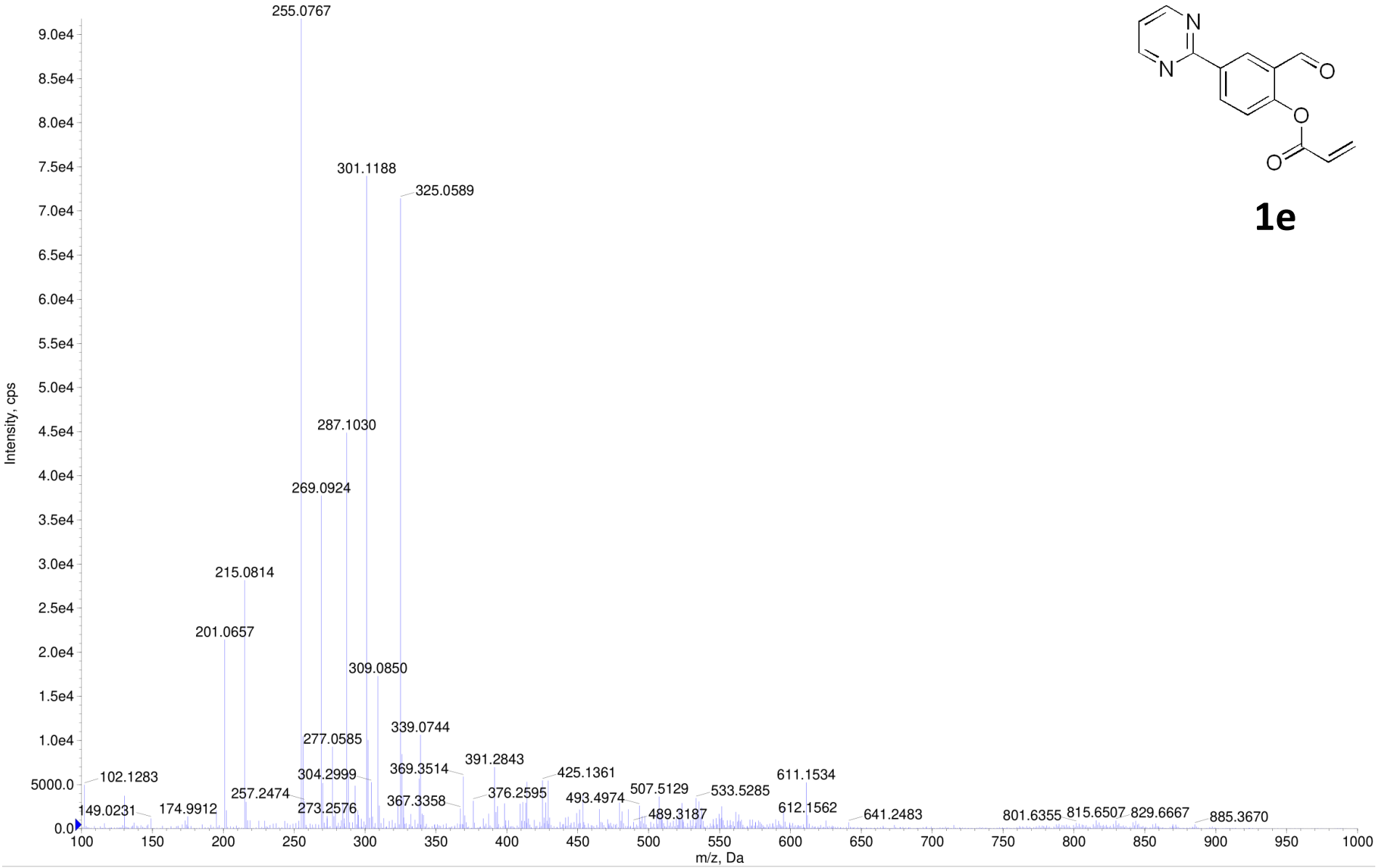
127.25
123.86
119.80
Chemical Shift (ppm)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m/z, Da
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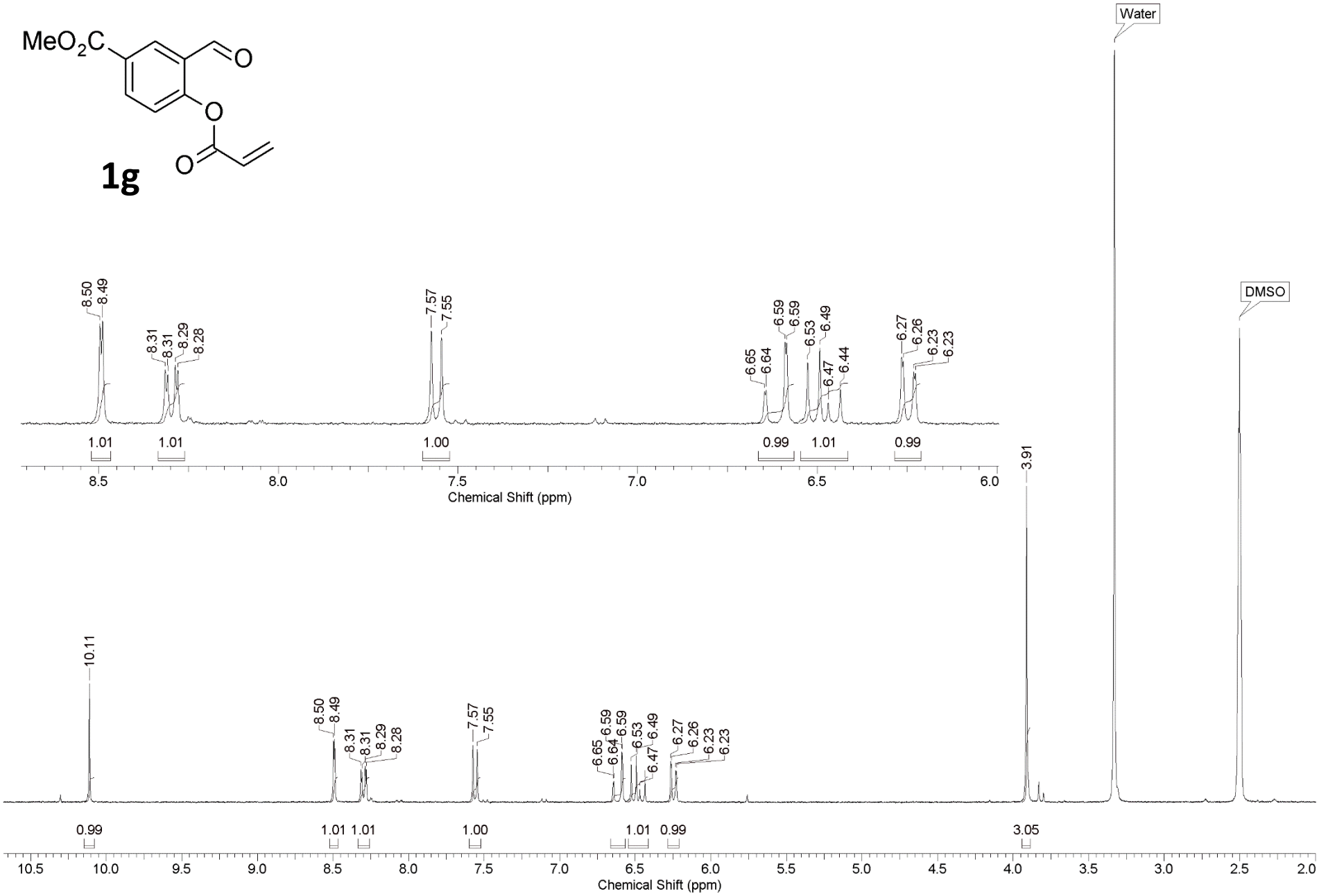
950
1000

1e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6.64
6.59
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6.53
6.49
6.47
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6.27
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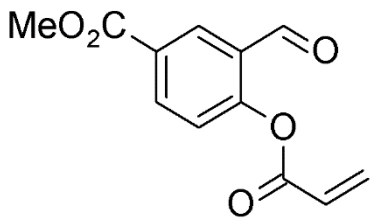
Chemical Shift (ppm)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124.55
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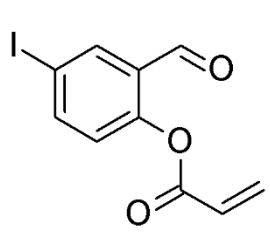
Chemical Shift (ppm)



1h

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1.01
8.0
7.5
7.0
6.5
6.0
Chemical Shift (ppm)
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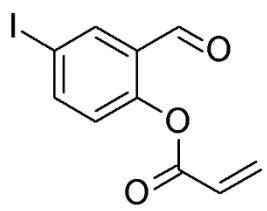
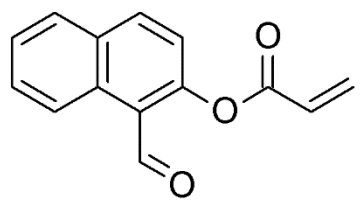
1.00
1.02
1.00
1.02
1.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)


I
O
O
O

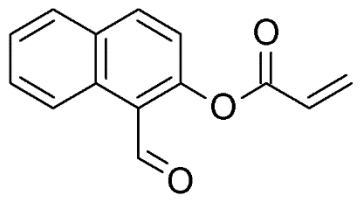
1h

DMSO
188.80
163.70
150.16
143.84
139.72
134.38
129.57
127.10
126.14
91.45
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
Chemical Shift (ppm)



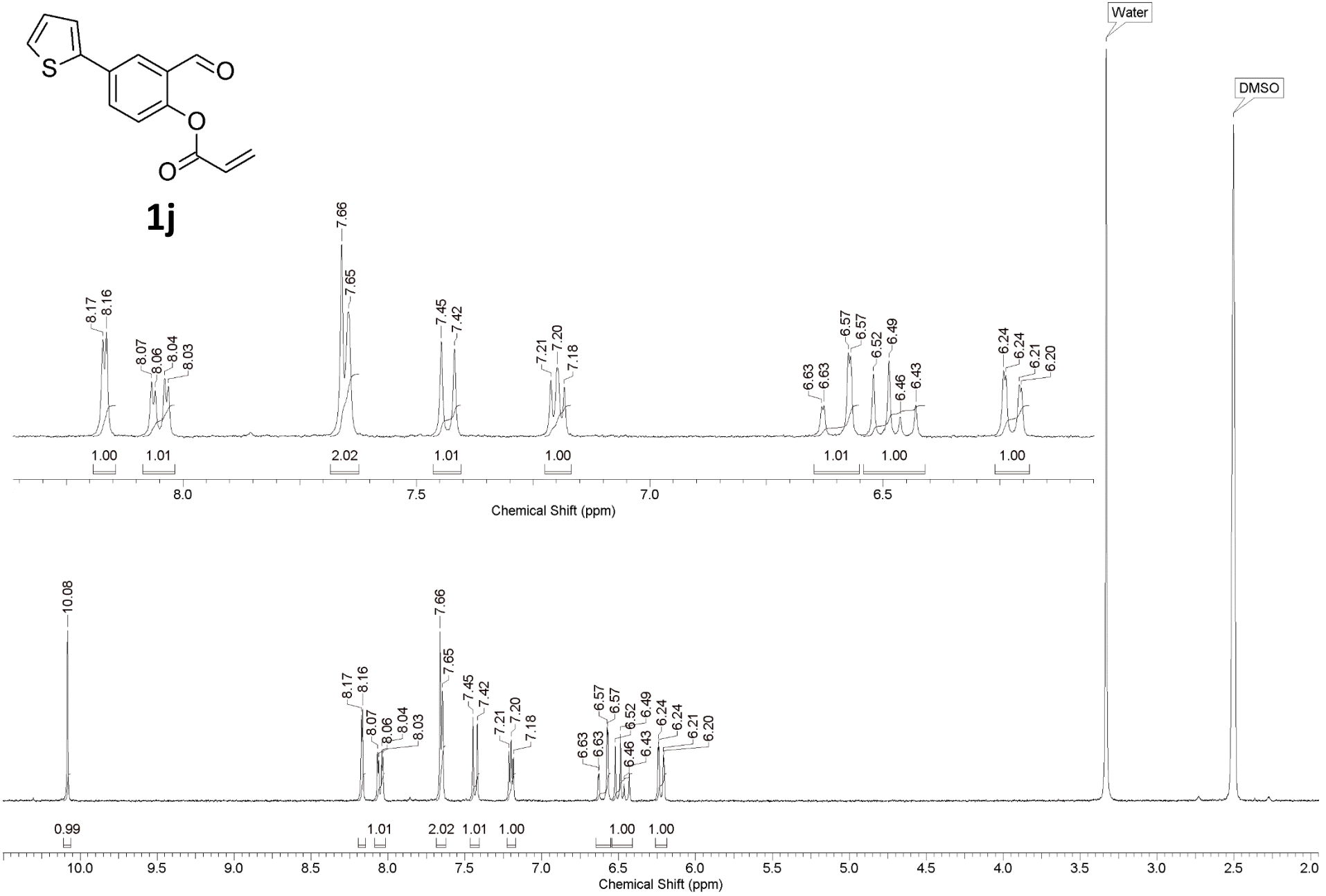
1i

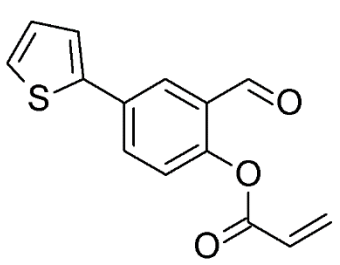
Water
DMSO
9.05
9.02
8.38
8.35
8.11
8.08
7.79
7.78
7.76
7.74
7.73
7.69
7.66
7.64
7.55
7.52
6.69
6.69
6.64
6.63
6.58
6.54
6.52
6.49
6.29
6.28
6.26
6.25
1.03
1.06
1.06
1.05
1.05
1.00
0.98
0.97
1.02
9.0
8.5
8.0
7.5
7.0
6.5
Chemical Shift (ppm)
10.62
0.98
1.03
1.06
1.06
1.05
1.00
0.97
1.02
11.0
10.5
10.0
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
Chemical Shift (ppm)



1i

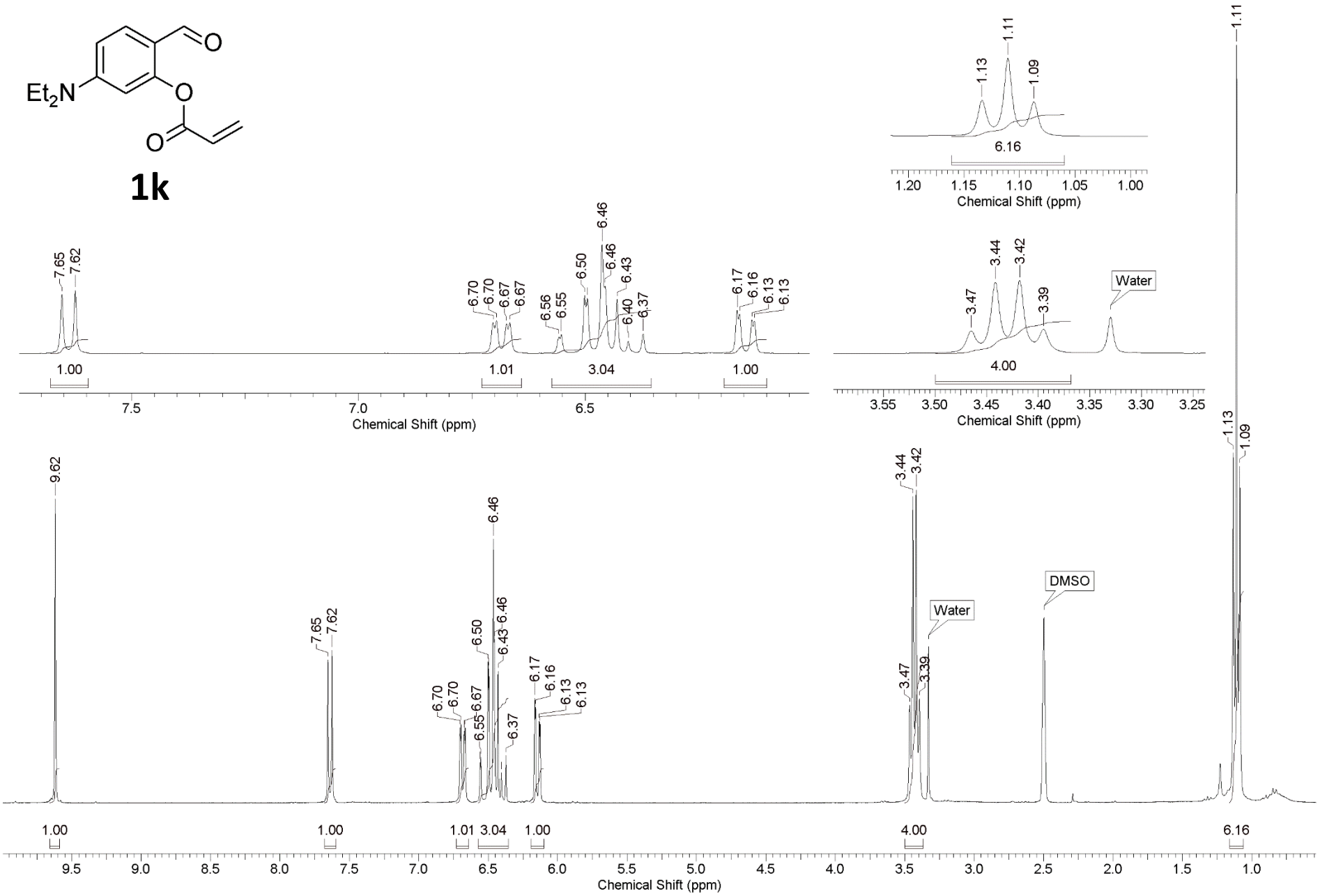
DMSO
136.68
134.69
131.41
130.30
129.61
128.78
127.05
126.70
124.25
122.19
121.03
138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119
Chemical Shift (ppm)
190.73
164.21
153.72
136.68
134.69
131.41
129.61
128.78
127.05
126.70
124.25
122.19
121.03
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32
Chemical Shift (ppm)

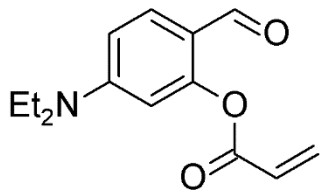

1j
Water
DMSO
10.08
8.17
8.16
8.07
8.06
8.04
8.03
7.66
7.65
7.45
7.42
7.21
7.20
7.18
6.63
6.63
6.57
6.57
6.52
6.49
6.46
6.43
6.24
6.24
6.21
6.20
0.99
1.01
2.02
1.01
1.00
1.00
1.00
Chemical Shift (ppm)


S
O
O
O

1j

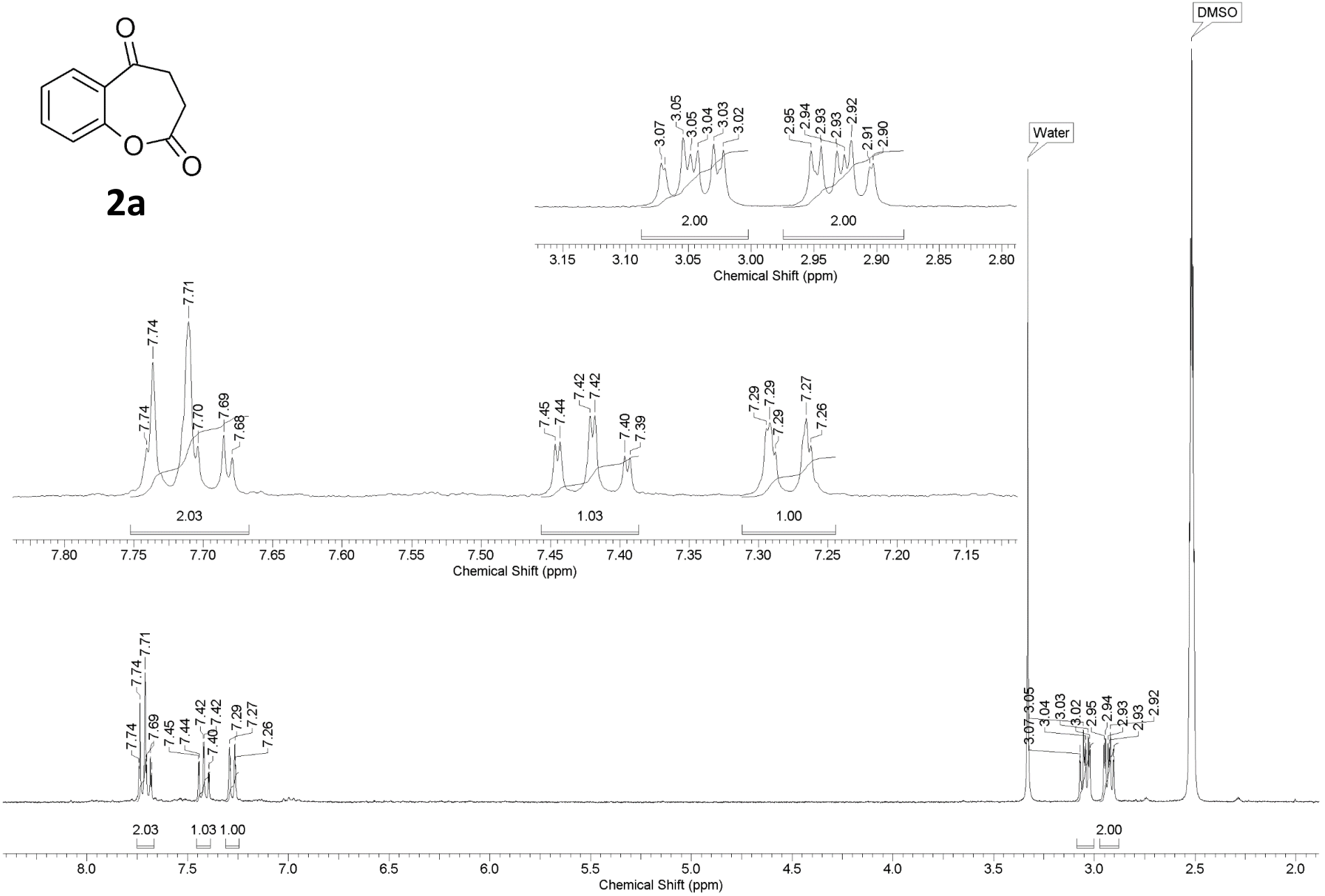
DMSO
134.22
132.40
131.97
128.78
128.27
127.87
127.22
126.81
125.01
124.63
135.0 134.5 134.0 133.5 133.0 132.5 132.0 131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5 125.0 124.5 124.0 123.5 123.0
Chemical Shift (ppm)
189.67
163.98
149.49
141.05
134.22
131.97
128.78
127.87
127.22
126.81
125.01
124.63
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32
Chemical Shift (ppm)

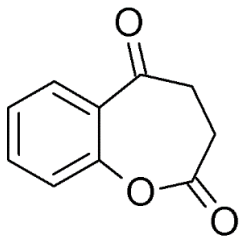

Et2N
O
O
O
1k
9.62
7.65
7.62
6.70
6.70
6.67
6.67
6.56
6.55
6.50
6.46
6.46
6.43
6.40
6.37
6.17
6.16
6.13
6.13
3.44
3.42
3.47
3.39
Water
DMSO
1.13
1.11
1.09
1.00
1.01
3.04
4.00
6.16
Chemical Shift (ppm)


Et2N
O
O
O

1k

DMSO
153.06
152.81
133.47
133.40
154
152
150
148
146
144
142
140
138
136
134
132
Chemical Shift (ppm)
186.02
163.97
153.06
152.81
133.47
133.40
127.65
115.53
108.58
104.41
44.12
12.27
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)


2a
DMSO
Water
3.07
3.05
3.05
3.04
3.03
3.02
2.95
2.94
2.93
2.93
2.92
2.91
2.90
2.00
2.00
Chemical Shift (ppm)
7.74
7.71
7.74
7.70
7.69
7.68
7.45
7.44
7.42
7.42
7.40
7.39
7.29
7.29
7.29
7.27
7.26
2.03
1.03
1.00
Chemical Shift (ppm)
7.74
7.71
7.74
7.69
7.45
7.44
7.42
7.40
7.42
7.29
7.27
7.26
3.07
3.05
3.04
3.03
3.02
2.95
2.94
2.93
2.93
2.92
2.03
1.03
1.00
2.00
Chemical Shift (ppm)

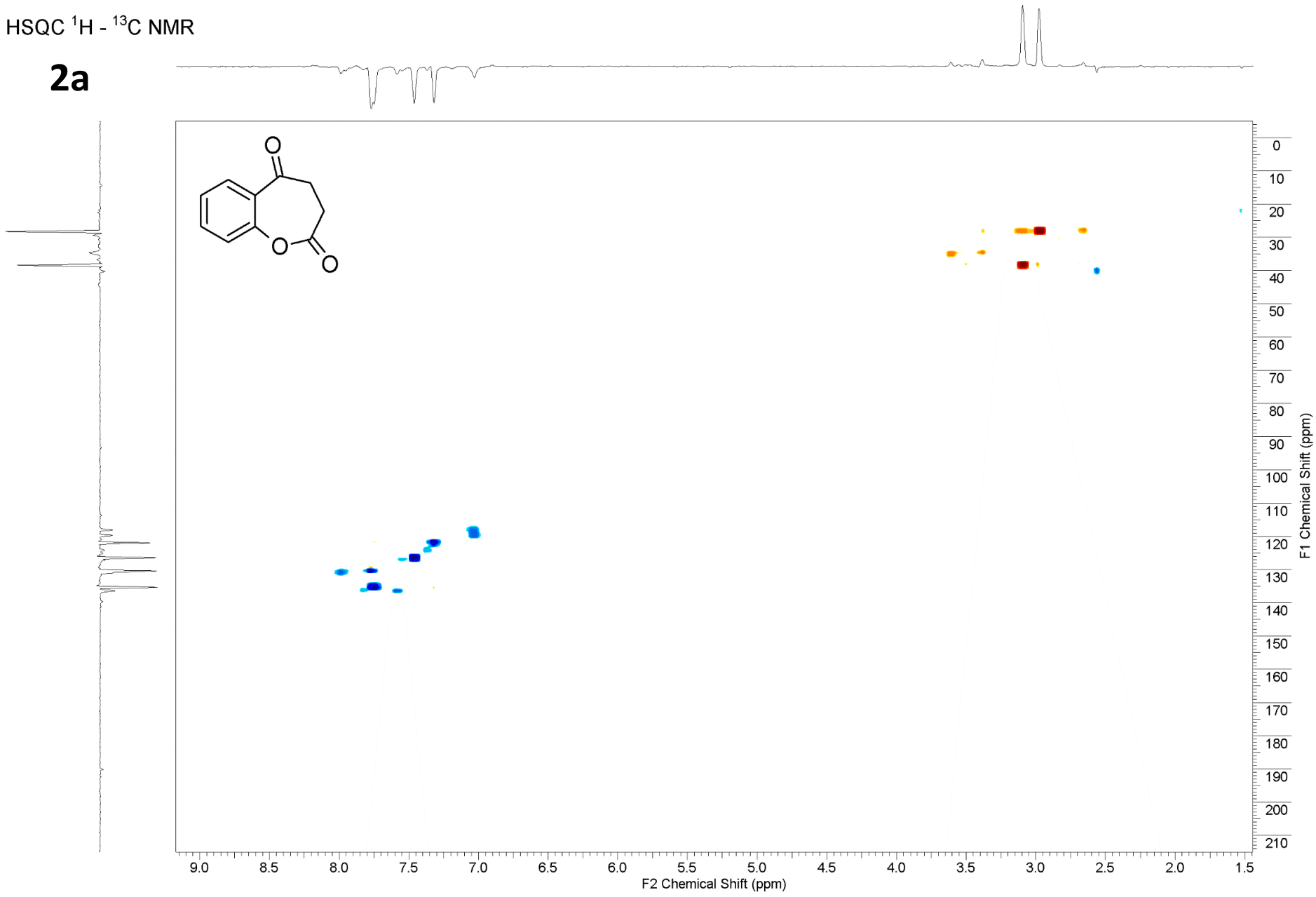


2a

DMSO
198.89
169.89
151.05
134.88
129.97
127.78
126.00
121.54
37.94
27.85
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
Chemical Shift (ppm)

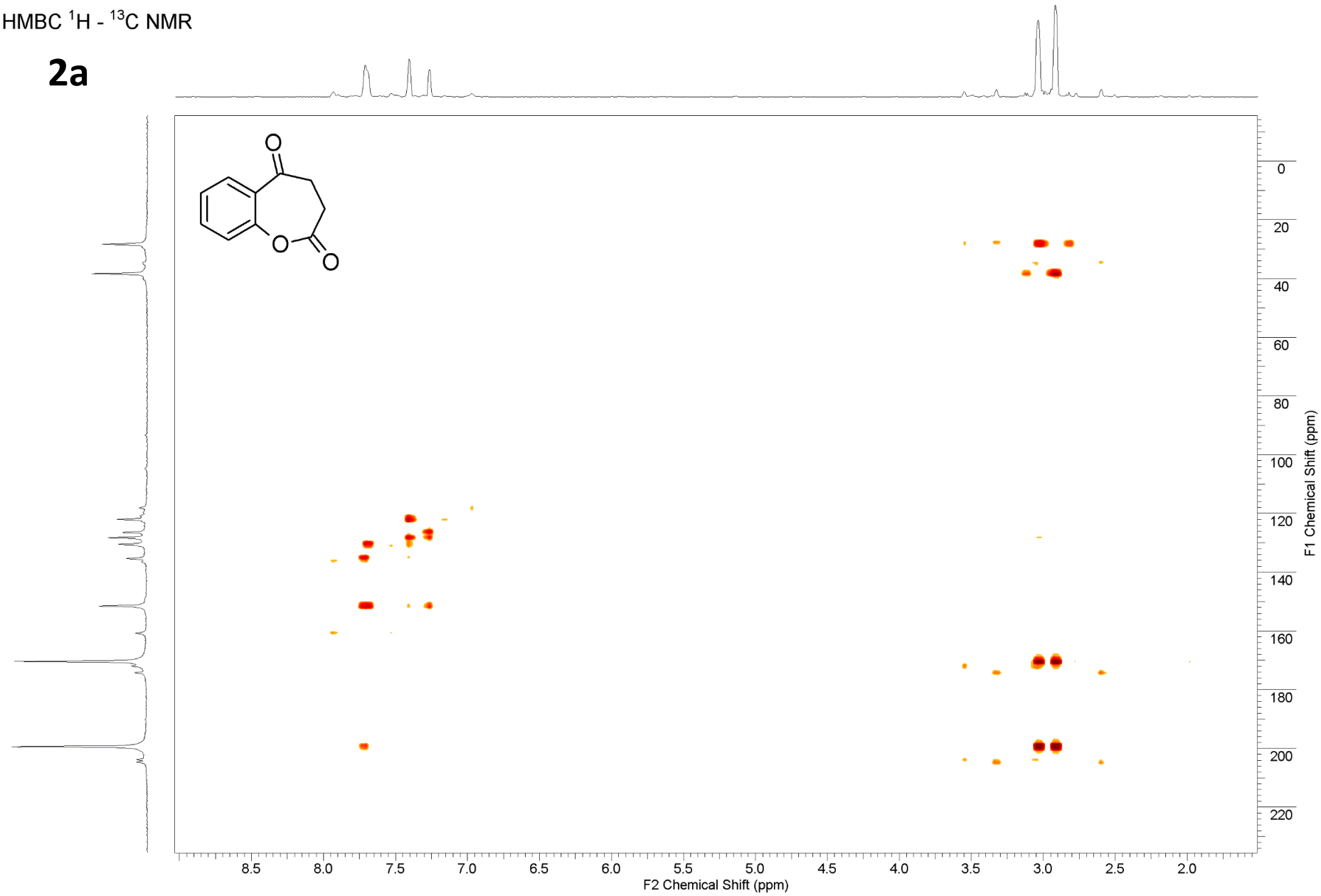
HSQC ^{1}H - ^{13}C NMR

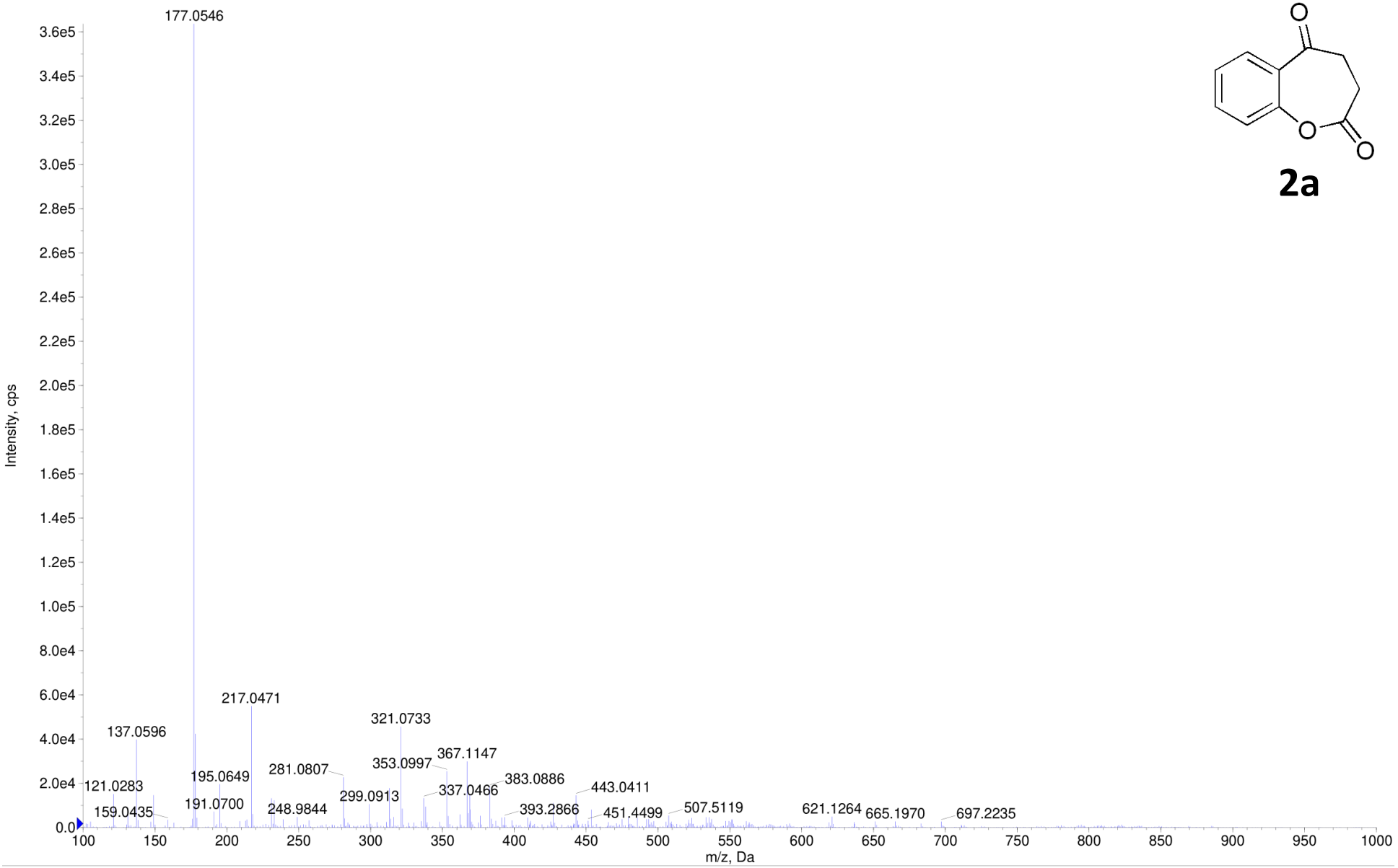
2a



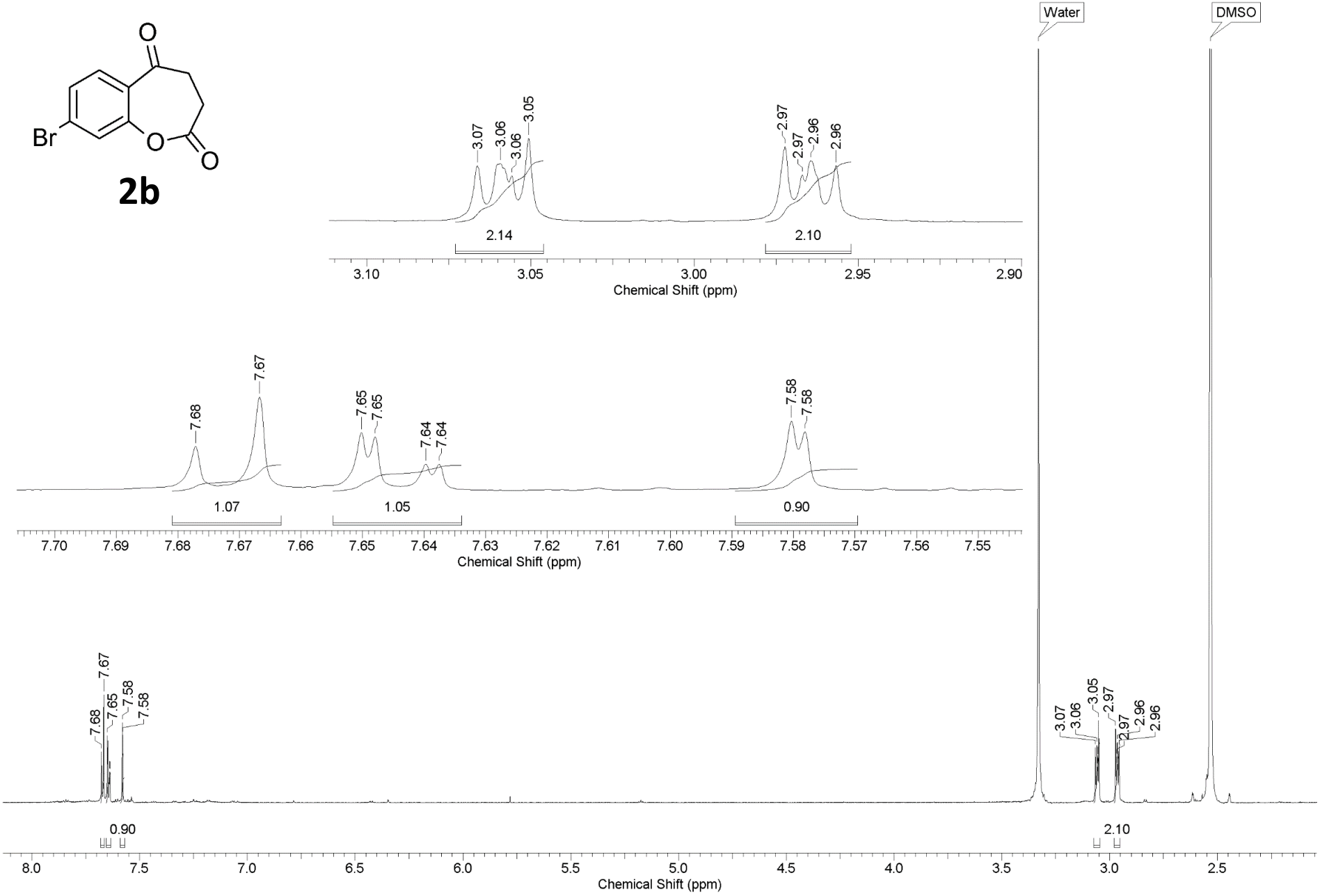
HMBC ^{1}H - ^{13}C NMR

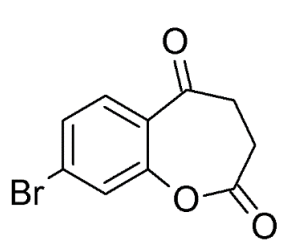
2a




177.0546
3.6e5
3.4e5
3.2e5
3.0e5
2.8e5
2.6e5
2.4e5
2.2e5
2.0e5
1.8e5
1.6e5
1.4e5
1.2e5
1.0e5
8.0e4
6.0e4
4.0e4
2.0e4
0.0
Intensity, cps
217.0471
321.0733
137.0596
367.1147
353.0997
281.0807
383.0886
195.0649
443.0411
121.0283
337.0466
299.0913
191.0700
159.0435
248.9844
393.2866
451.4499
507.5119
621.1264
665.1970
697.2235
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
m/z, Da

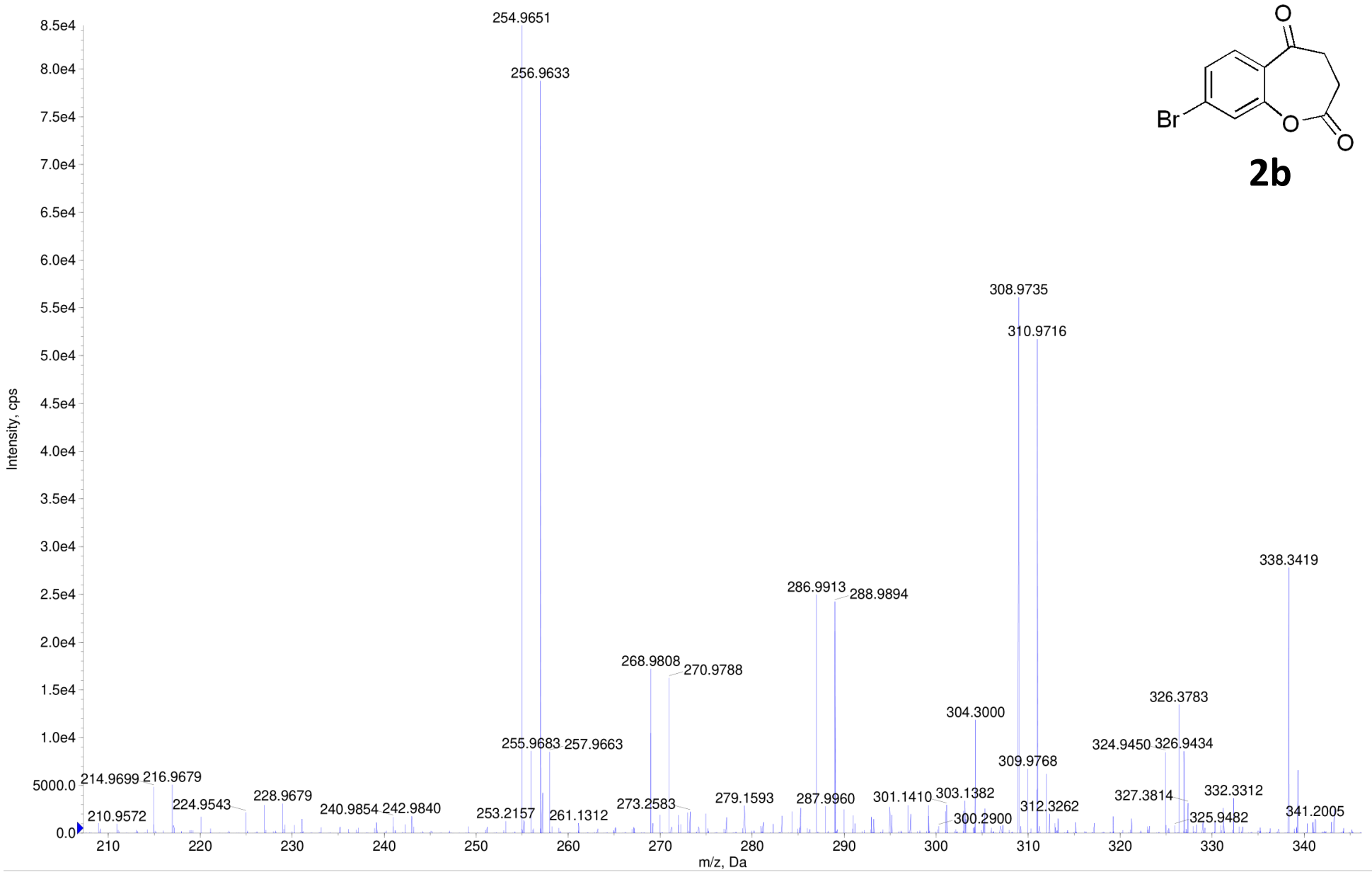
2a

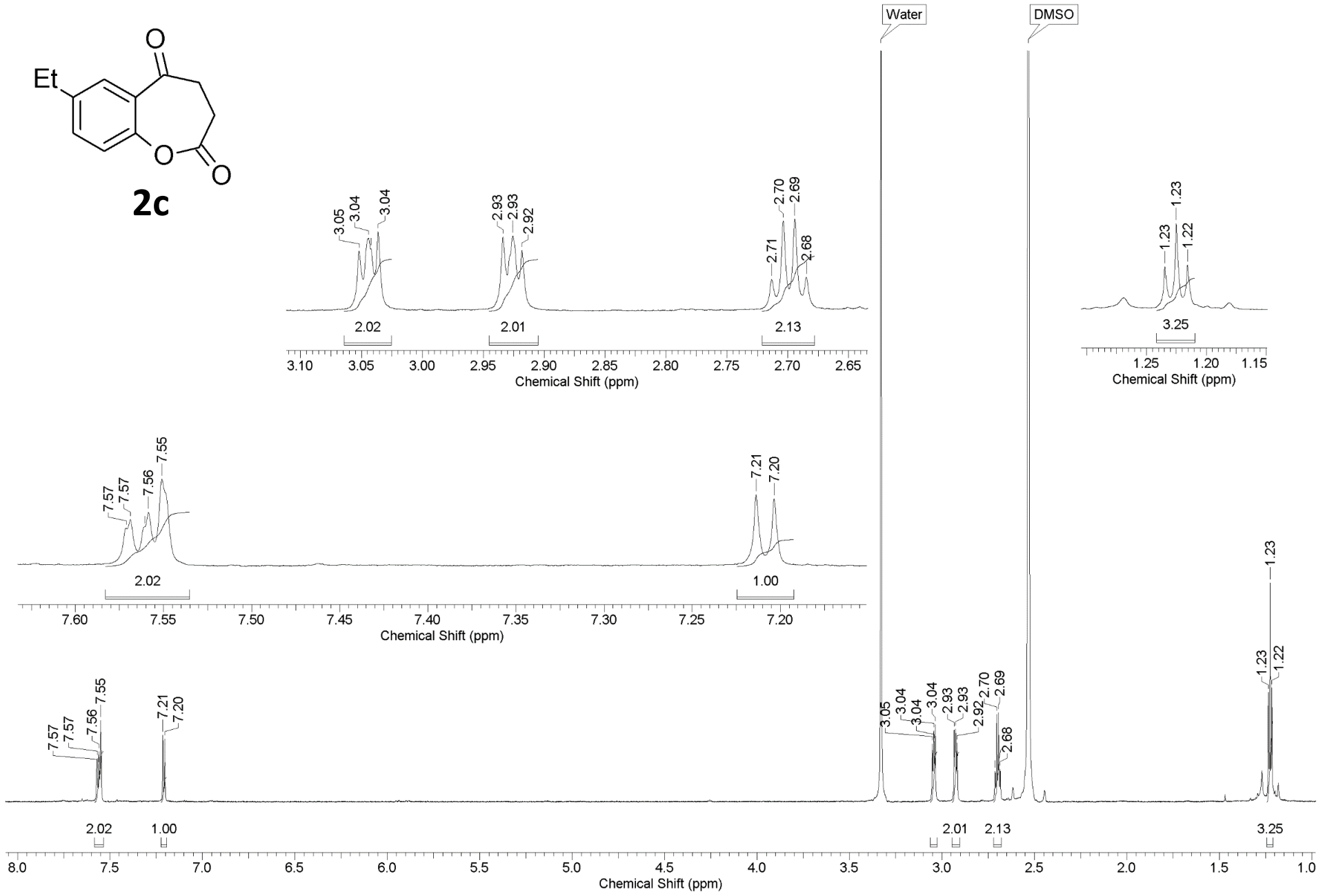

Br
O
O
O
2b
Water
DMSO
3.07
3.06
3.06
3.05
2.97
2.97
2.96
2.96
2.14
2.10
3.10
3.05
3.00
2.95
2.90
Chemical Shift (ppm)
7.68
7.67
7.65
7.65
7.64
7.64
7.58
7.58
1.07
1.05
0.90
7.70
7.69
7.68
7.67
7.66
7.65
7.64
7.63
7.62
7.61
7.60
7.59
7.58
7.57
7.56
7.55
Chemical Shift (ppm)
7.68
7.67
7.65
7.58
7.58
3.07
3.06
3.05
2.97
2.97
2.96
2.96
0.90
2.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
Chemical Shift (ppm)

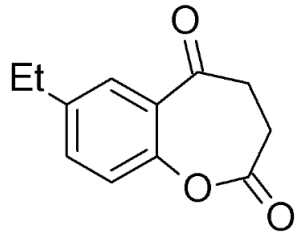

O
Br
O
O

2b

DMSO
131.68
129.01
127.46
126.94
124.55
133.0 132.5 132.0 131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5 125.0 124.5 124.0 123.5 123.0 122.5
Chemical Shift (ppm)
197.98
169.31
151.47
131.68
129.01
126.94
124.55
37.67
27.64
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24
Chemical Shift (ppm)

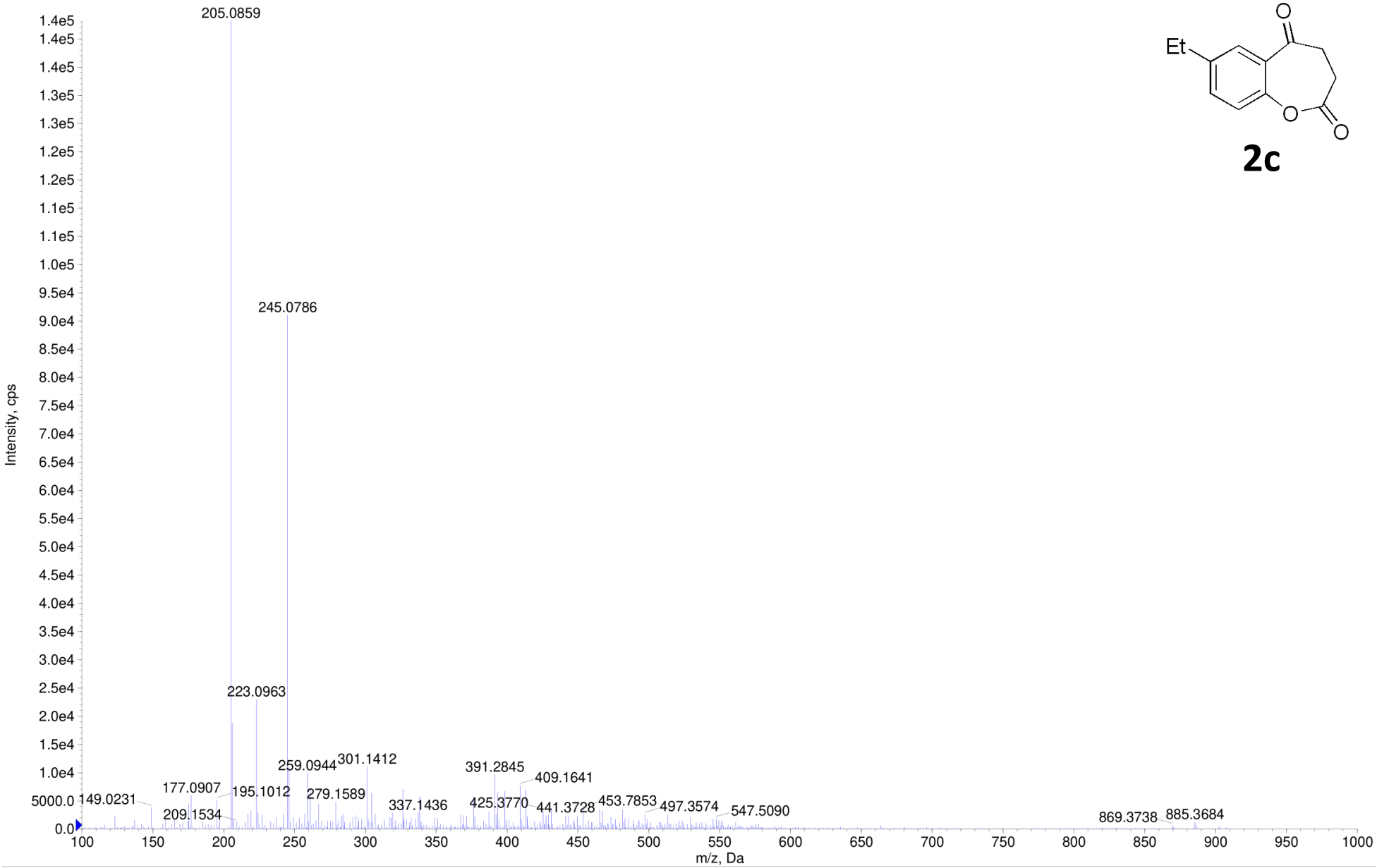

254.9651
256.9633
308.9735
310.9716
338.3419
286.9913
288.9894
268.9808
270.9788
326.3783
304.3000
255.9683
257.9663
324.9450
326.9434
309.9768
214.9699
216.9679
224.9543
228.9679
210.9572
240.9854
242.9840
253.2157
261.1312
273.2583
279.1593
287.9960
301.1410
303.1382
300.2900
312.3262
327.3814
332.3312
325.9482
341.2005
Intensity, cps
m/z, Da
8.5e4
8.0e4
7.5e4
7.0e4
6.5e4
6.0e4
5.5e4
5.0e4
4.5e4
4.0e4
3.5e4
3.0e4
2.5e4
2.0e4
1.5e4
1.0e4
5000.0
0.0
210
220
230
240
250
260
270
280
290
300
310
320
330
340
Br
O
O
O
2b

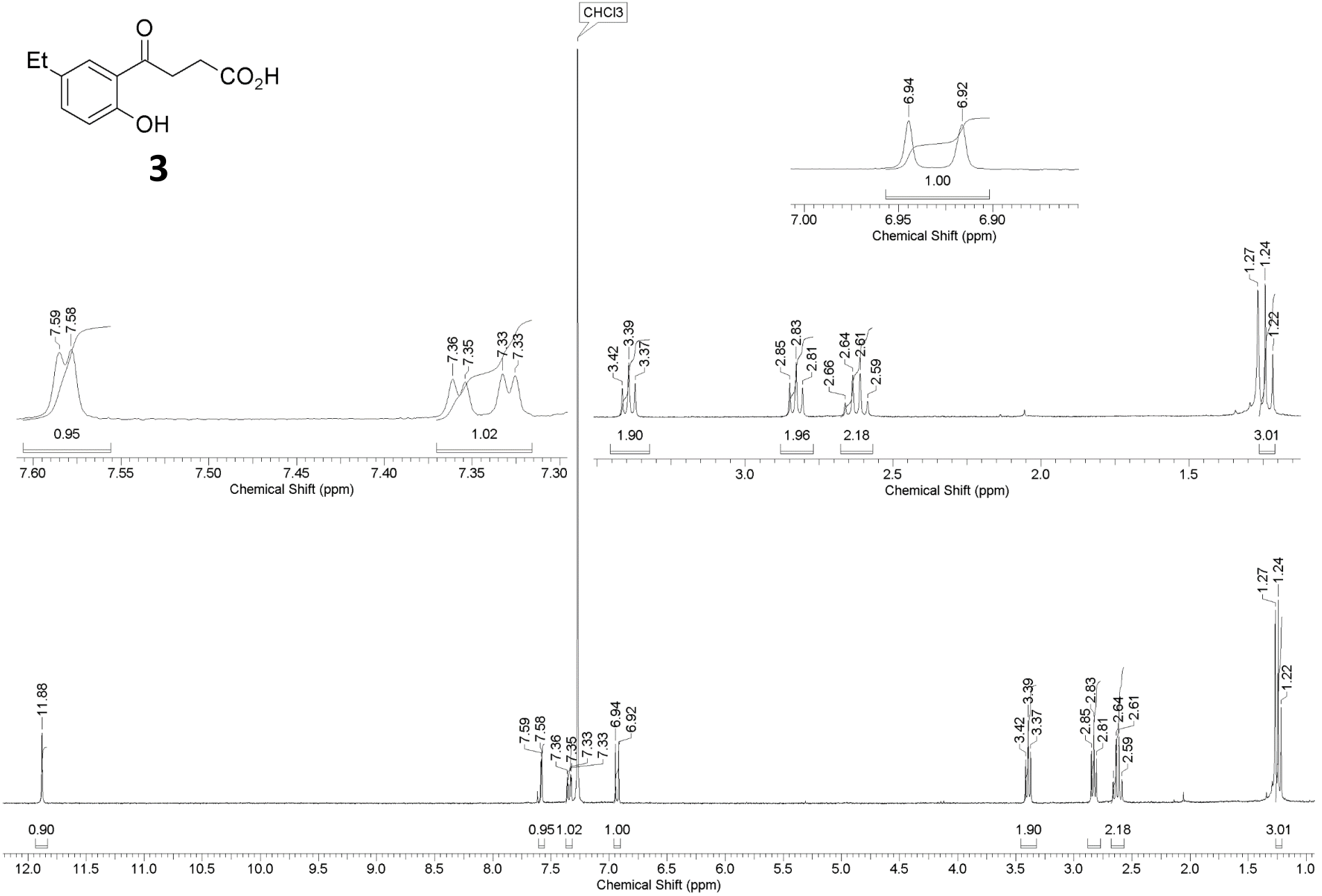

Et
O
O
O
2c
Water
DMSO
3.05
3.04
3.04
2.93
2.93
2.92
2.71
2.70
2.69
2.68
2.02
2.01
2.13
Chemical Shift (ppm)
1.23
1.23
1.22
3.25
Chemical Shift (ppm)
7.57
7.57
7.56
7.55
7.21
7.20
2.02
1.00
Chemical Shift (ppm)
2.02
1.00
2.01
2.13
3.25
Chemical Shift (ppm)

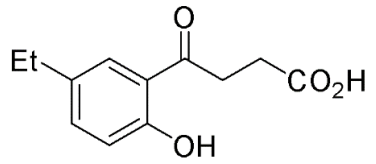

Et
O
O
O

2c

DMSO
198.98
170.11
149.25
141.51
134.28
128.64
127.45
121.49
37.94
27.88
27.14
15.28
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)

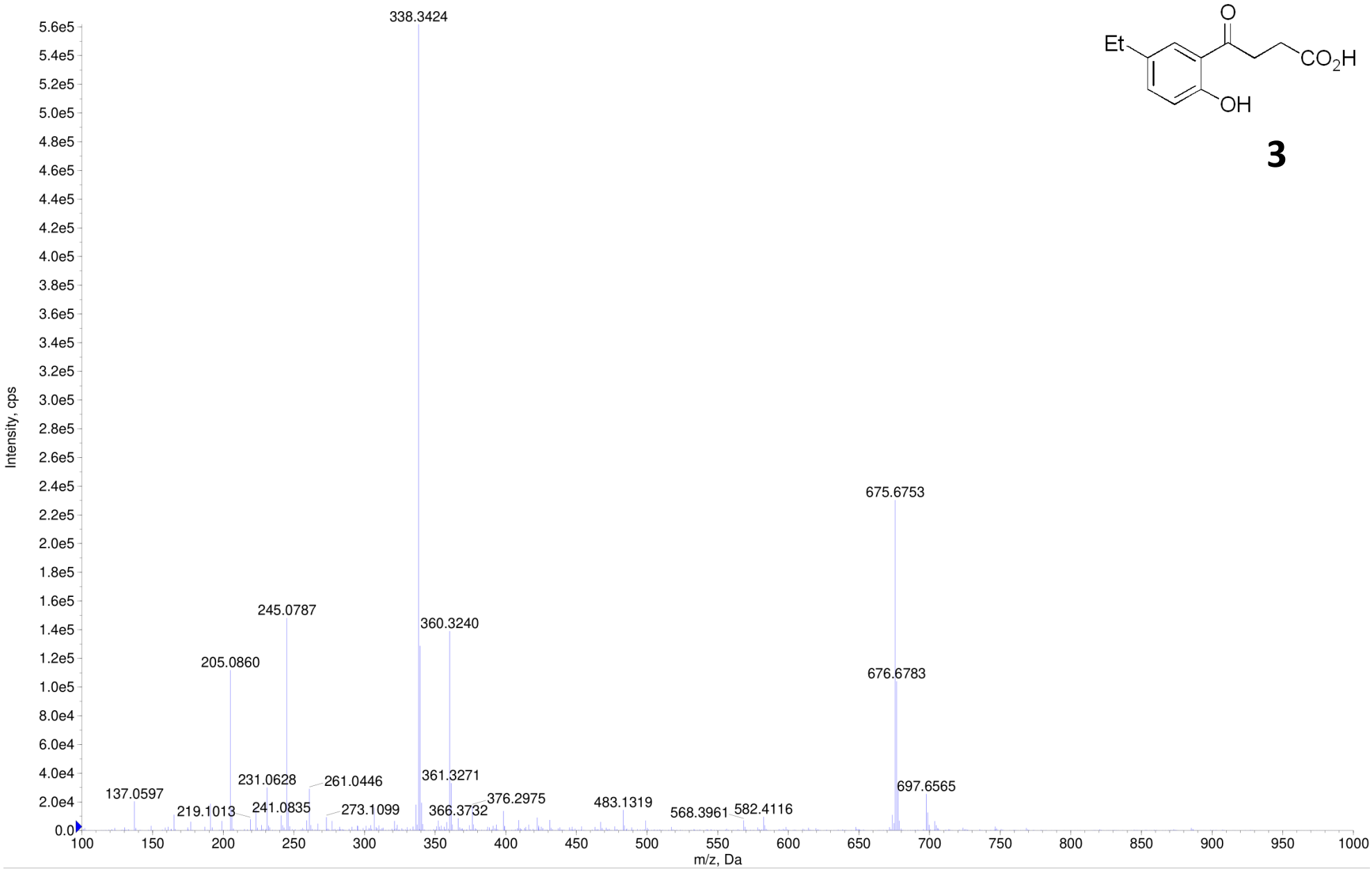

205.0859
245.0786
223.0963
259.0944
301.1412
391.2845
409.1641
177.0907
195.1012
279.1589
337.1436
425.3770
441.3728
453.7853
497.3574
547.5090
149.0231
209.1534
869.3738
885.3684
Intensity, cps
m/z, Da
Et
O
O
O
2c


Et
O
CO2H
OH
3
CHCl3
11.88
7.59
7.58
7.36
7.35
7.33
7.33
6.94
6.92
3.42
3.39
3.37
2.85
2.83
2.81
2.66
2.64
2.61
2.59
1.27
1.24
1.22
0.90
0.95
1.02
1.00
1.90
2.18
3.01
Chemical Shift (ppm)


O
Et
CO2H
OH

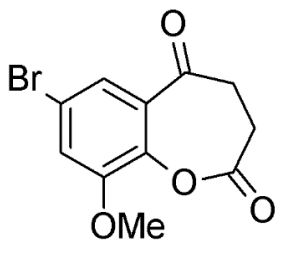
3

CDCl3
203.66
178.10
160.47
136.62
134.87
128.36
118.91
118.50
33.00
28.13
27.78
15.87
208 200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16
Chemical Shift (ppm)

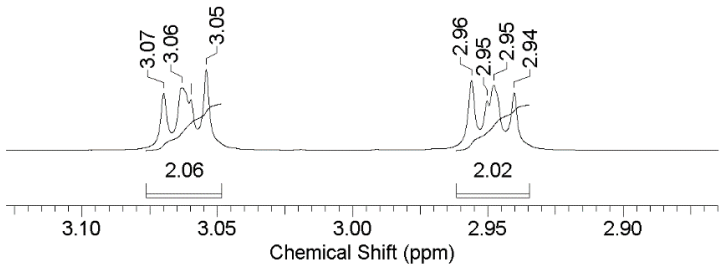

338.3424
675.6753
676.6783
245.0787
360.3240
205.0860
231.0628
261.0446
361.3271
137.0597
219.1013
241.0835
273.1099
366.3732
376.2975
483.1319
568.3961
582.4116
697.6565
Intensity, cps
m/z, Da
5.6e5
5.4e5
5.2e5
5.0e5
4.8e5
4.6e5
4.4e5
4.2e5
4.0e5
3.8e5
3.6e5
3.4e5
3.2e5
3.0e5
2.8e5
2.6e5
2.4e5
2.2e5
2.0e5
1.8e5
1.6e5
1.4e5
1.2e5
1.0e5
8.0e4
6.0e4
4.0e4
2.0e4
0.0
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000

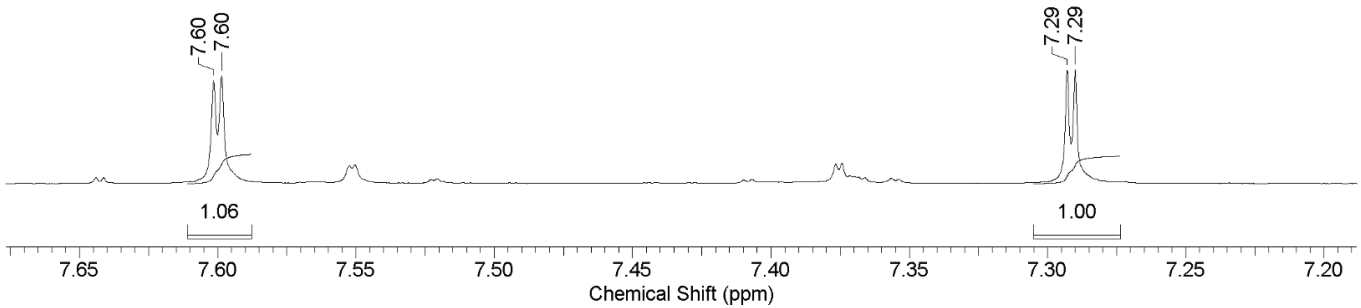
Et
O
CO2H
OH

3

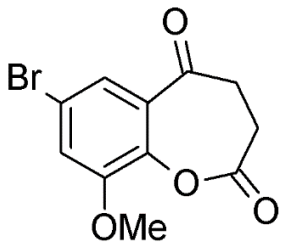

O
Br
O
O
OMe

2d


3.07
3.06
3.05
2.96
2.95
2.95
2.94
2.06
2.02
3.10
3.05
3.00
2.95
2.90
Chemical Shift (ppm)


7.60
7.60
7.29
7.29
1.06
1.00
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
Chemical Shift (ppm)

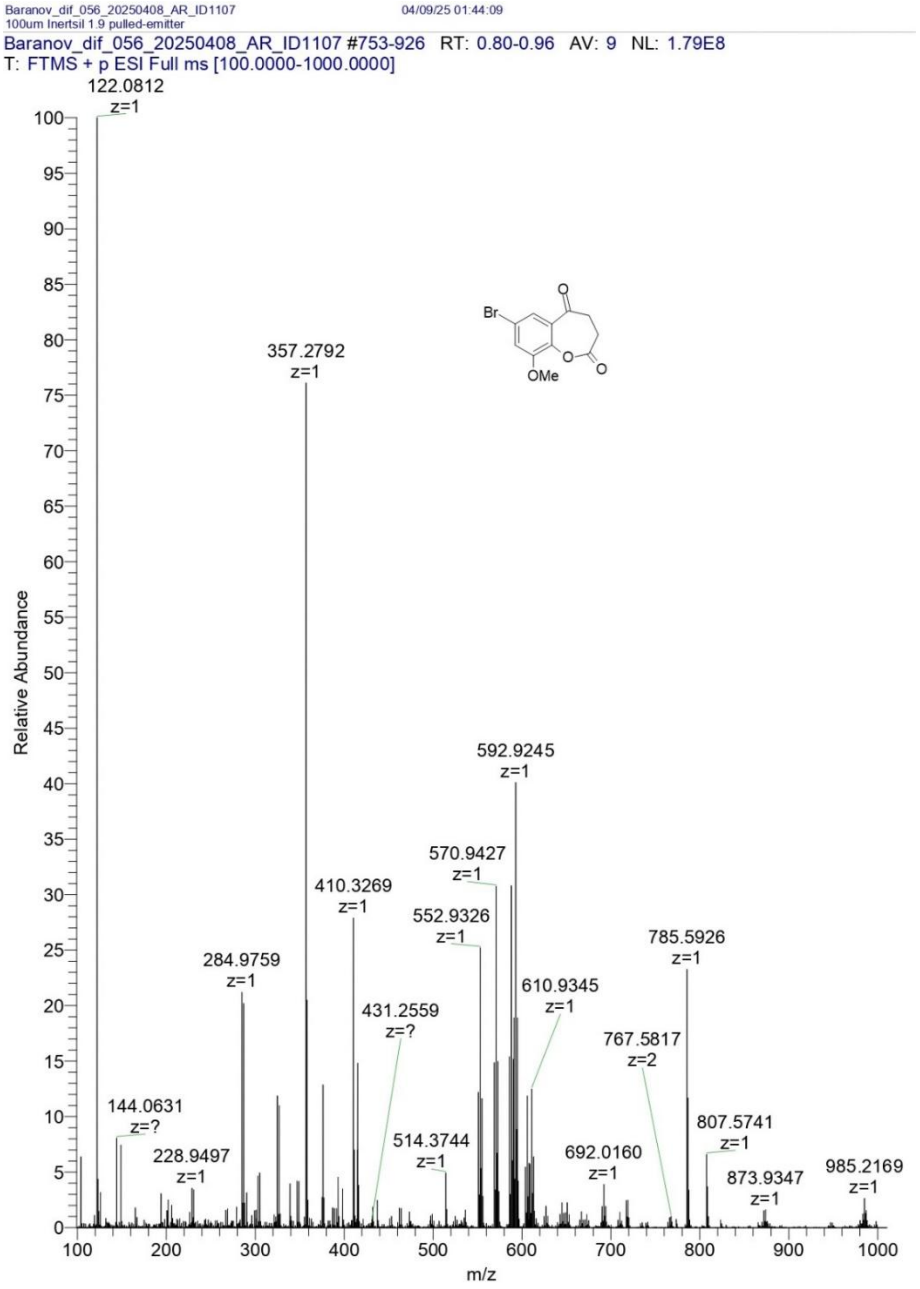
Water
DMSO
3.92
7.60
7.60
7.29
7.29
3.07
3.06
3.05
2.96
2.95
2.95
2.94
1.06
1.00
3.11
2.06
2.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
Chemical Shift (ppm)

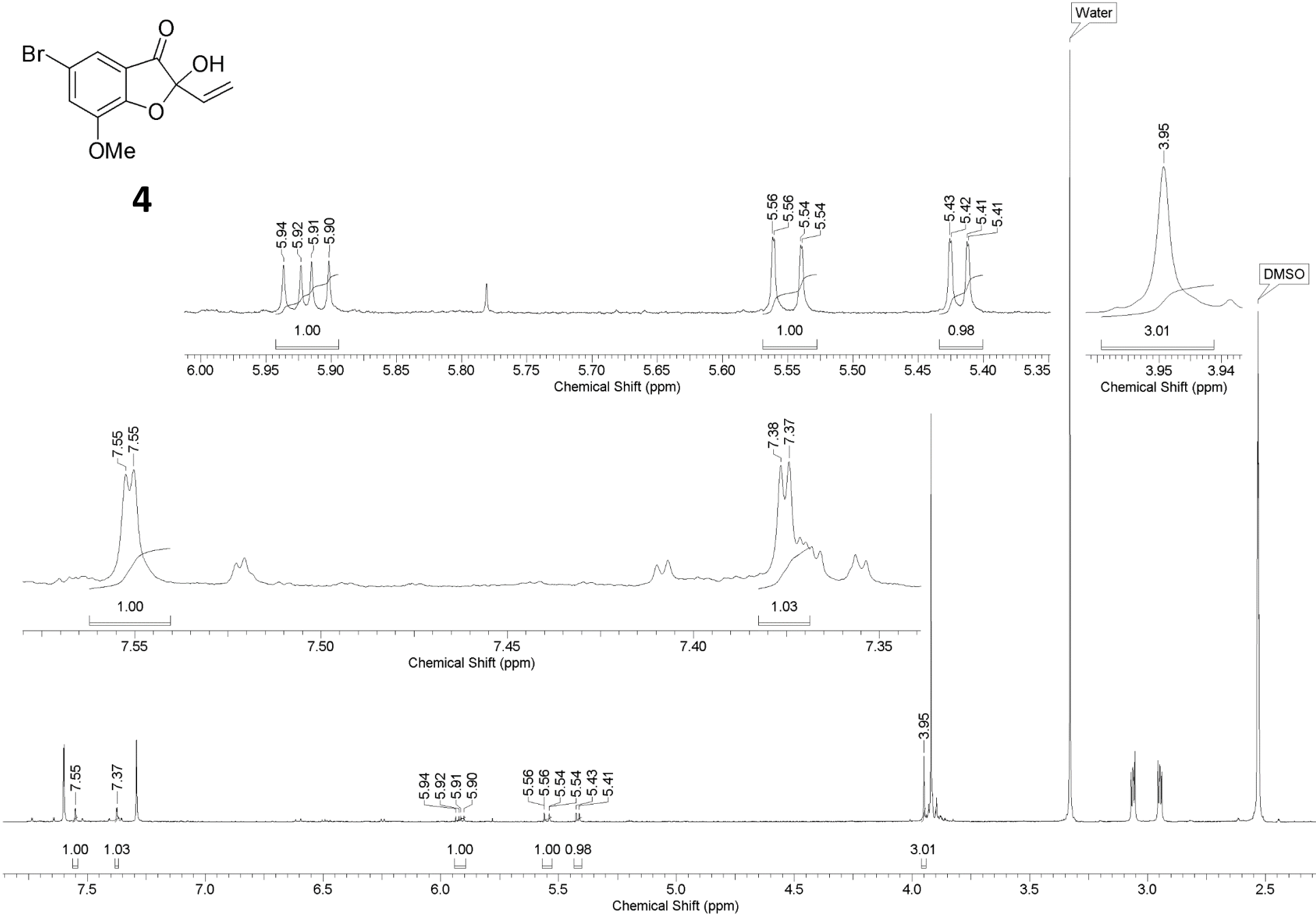

Br
O
O
O
OMe

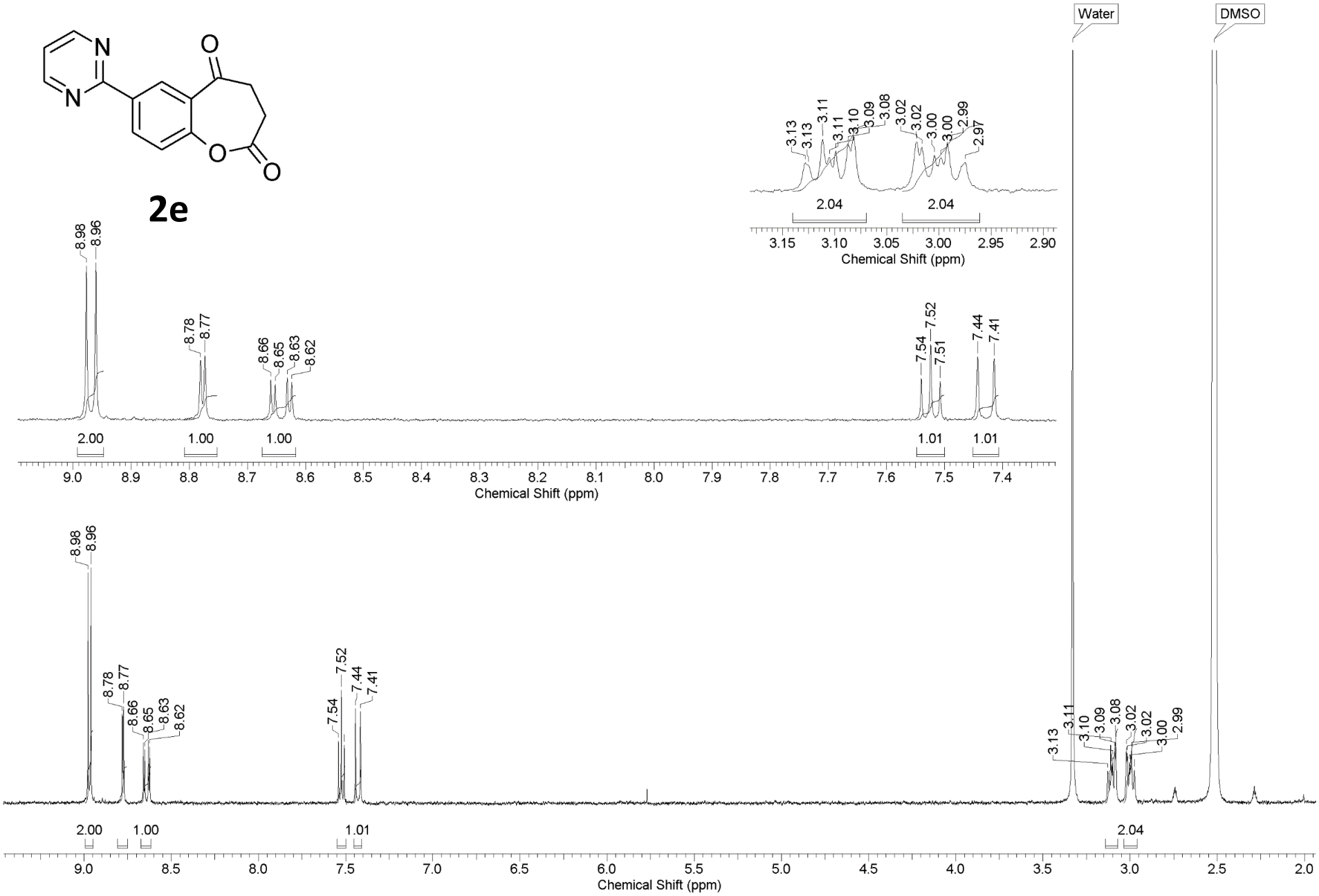
2d

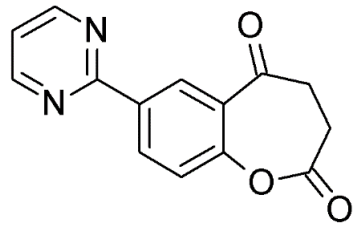
DMSO
198.07
169.40
151.24
139.80
130.20
122.32
119.82
117.97
56.81
38.07
27.62
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
Chemical Shift (ppm)

2d


Baranov_dif_056_20250408_AR_ID1107
100um Inertsil 1.9 pulled-emitter
04/09/25 01:44:09
Baranov_dif_056_20250408_AR_ID1107 #753-926 RT: 0.80-0.96 AV: 9 NL: 1.79E8
T: FTMS + p ESI Full ms [100.0000-1000.0000]
122.0812 z=1
357.2792 z=1
592.9245 z=1
570.9427 z=1
410.3269 z=1
552.9326 z=1
785.5926 z=1
284.9759 z=1
610.9345 z=1
431.2559 z=?
767.5817 z=2
144.0631 z=?
807.5741 z=1
514.3744 z=1
692.0160 z=1
228.9497 z=1
873.9347 z=1
985.2169 z=1
Br
O
O
O
OMe
Relative Abundance
m/z

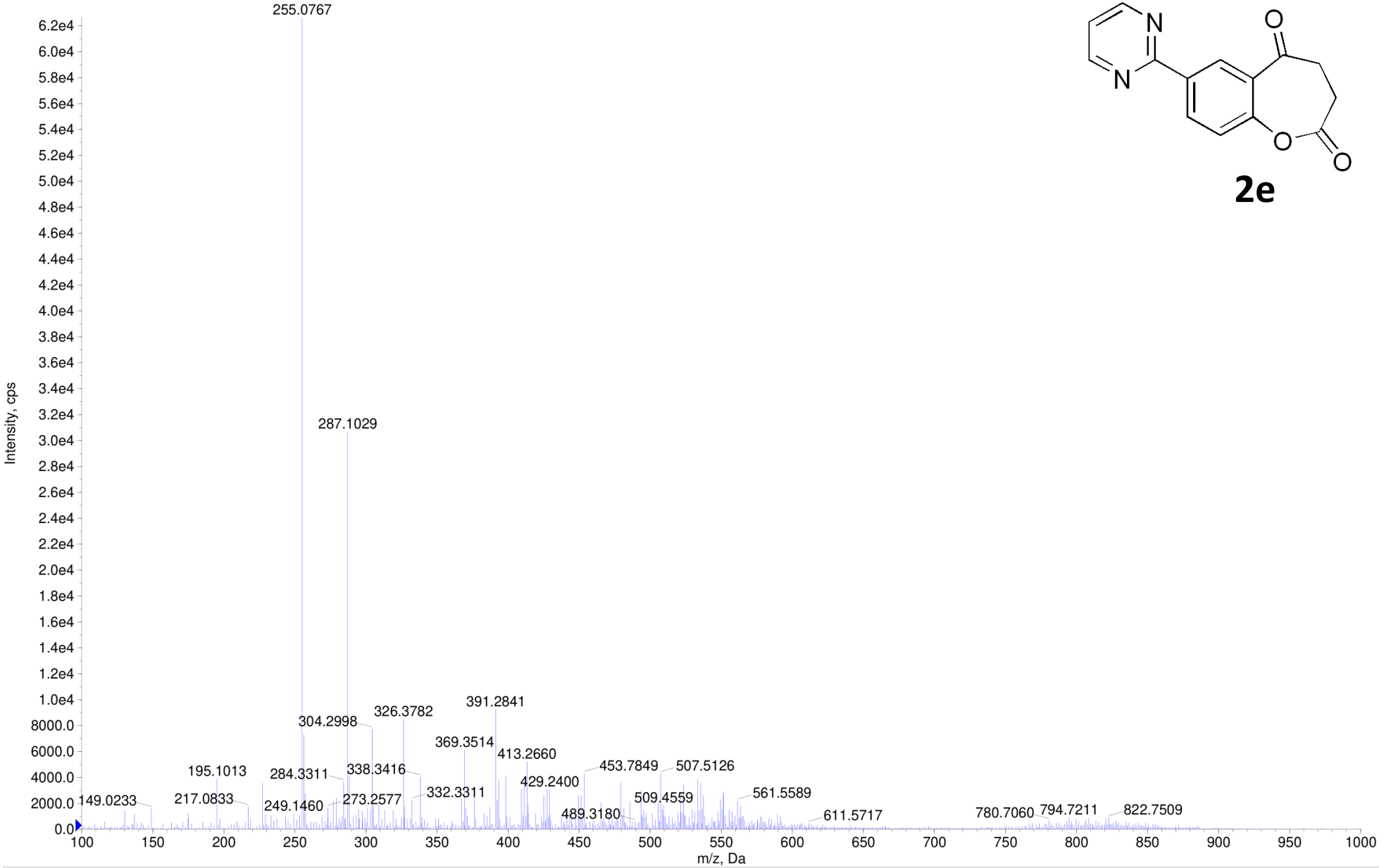

Br
O
OH
O
OMe
4
Water
DMSO
5.94
5.92
5.91
5.90
5.56
5.56
5.54
5.54
5.43
5.42
5.41
5.41
3.95
1.00
1.00
0.98
3.01
6.00
5.95
5.90
5.85
5.80
5.75
5.70
5.65
5.60
5.55
5.50
5.45
5.40
5.35
3.95
3.94
Chemical Shift (ppm)
7.55
7.55
7.38
7.37
1.00
1.03
7.55
7.50
7.45
7.40
7.35
Chemical Shift (ppm)
7.55
7.37
5.94
5.92
5.91
5.90
5.56
5.56
5.54
5.54
5.43
5.41
3.95
1.00
1.03
1.00
1.00
0.98
3.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
Chemical Shift (ppm)


2e
Water
DMSO
Chemical Shift (ppm)
Chemical Shift (ppm)
Chemical Shift (ppm)


N
N
O
O
O

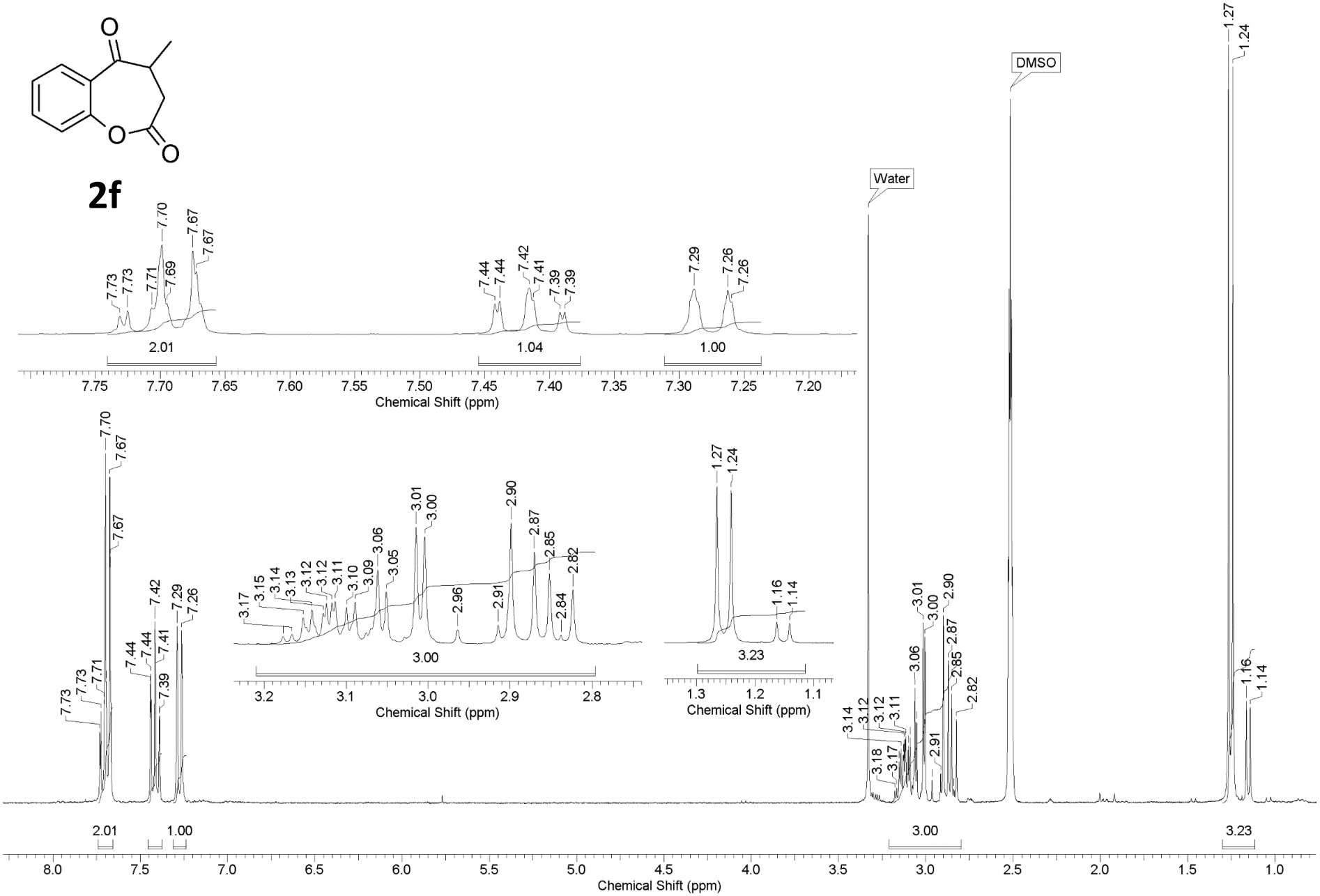
2e

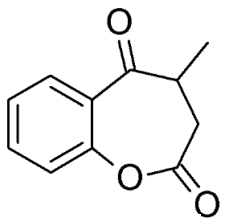
DMSO
198.46
169.54
161.64
157.92
152.73
134.61
133.43
129.65
127.87
122.35
120.31
37.72
27.83
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
Chemical Shift (ppm)


255.0767
287.1029
304.2998
326.3782
391.2841
369.3514
413.2660
453.7849
507.5126
429.2400
561.5589
509.4559
489.3180
611.5717
780.7060
794.7211
822.7509
195.1013
284.3311
338.3416
332.3311
273.2577
249.1460
217.0833
149.0233
Intensity, cps
m/z, Da

N
N
O
O
O

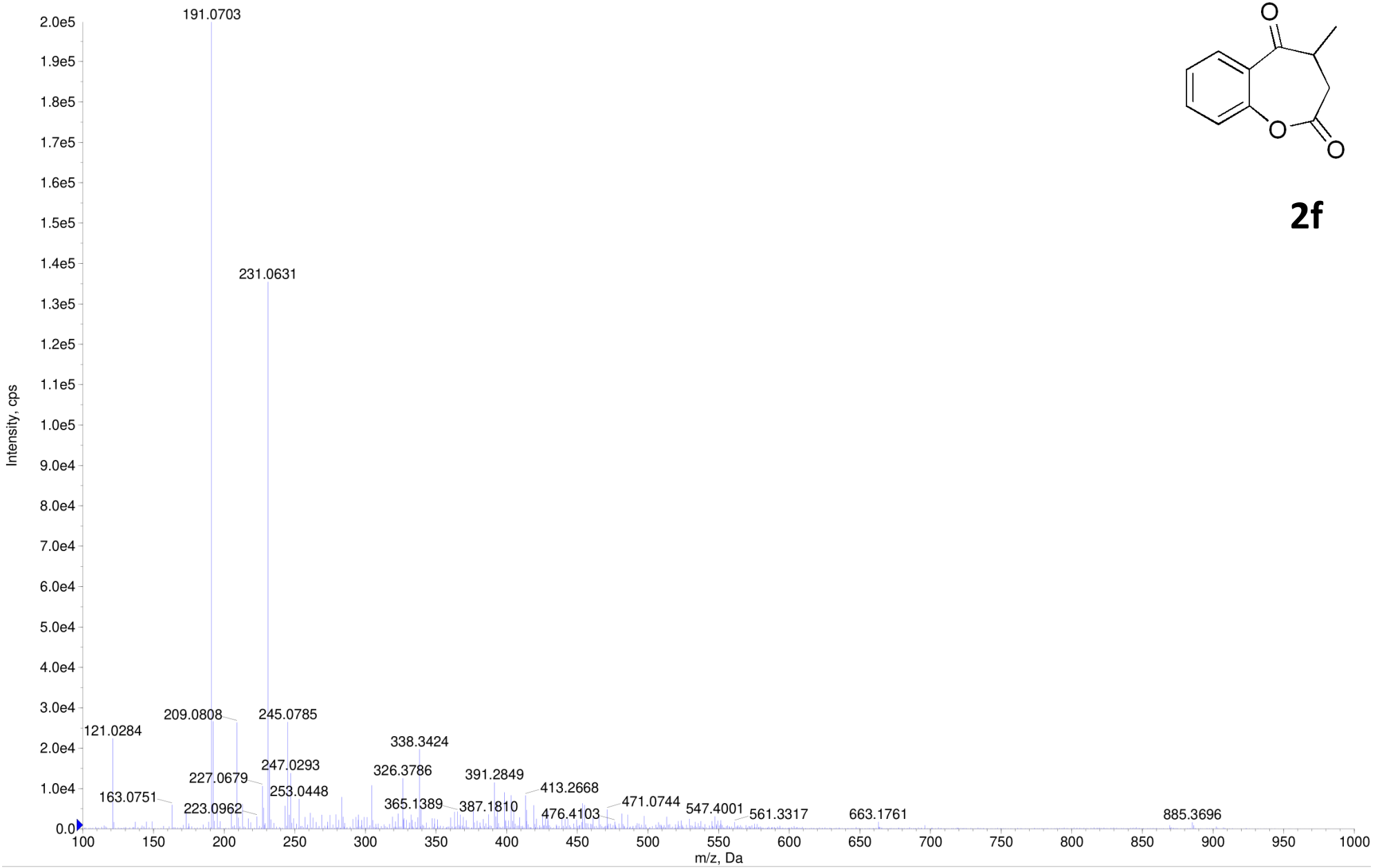
2e


2f
Water
DMSO
Chemical Shift (ppm)

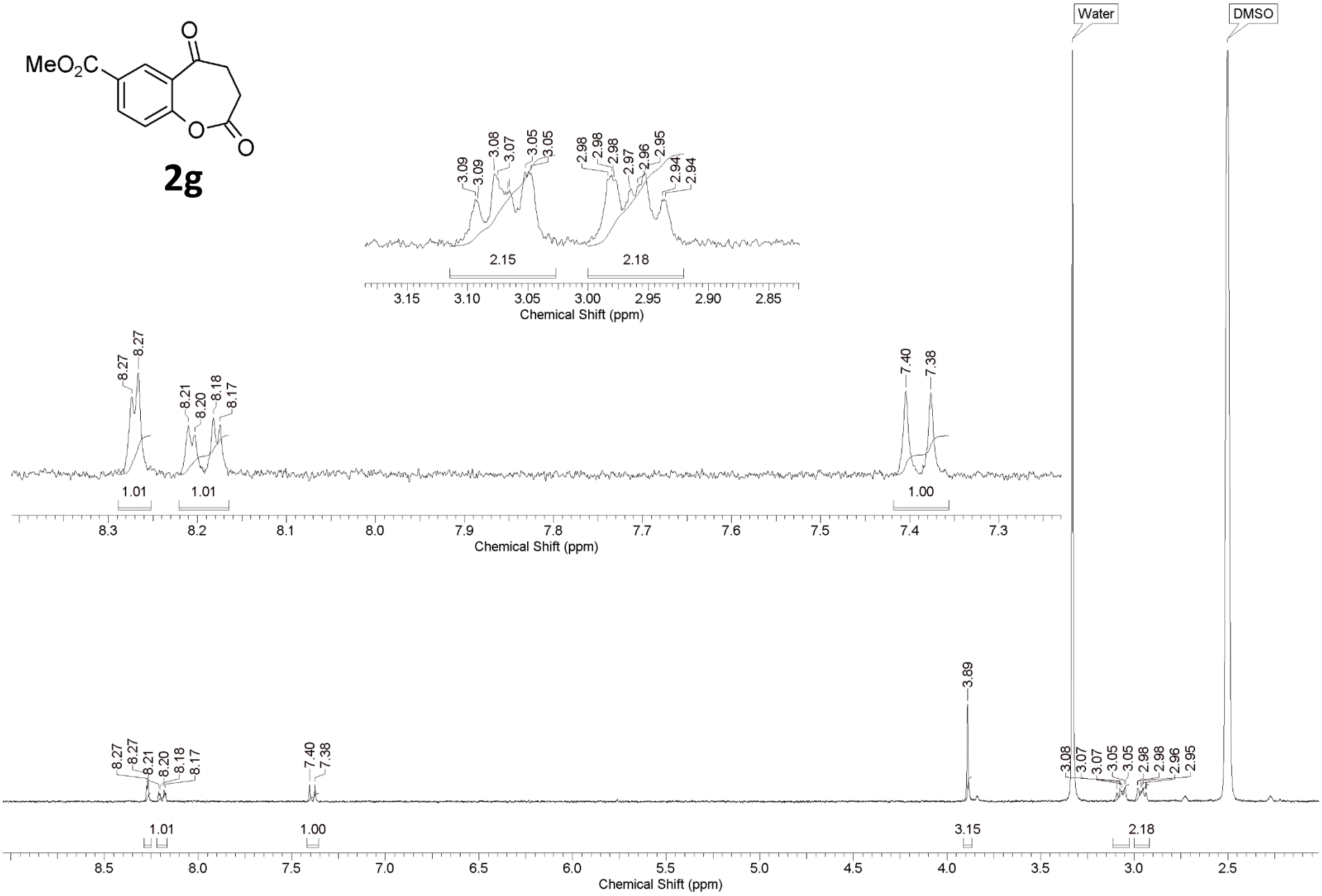


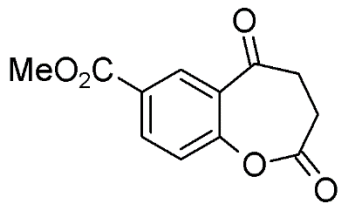
2f

DMSO
202.21
168.79
150.66
134.69
130.04
128.07
126.03
121.23
42.53
34.81
16.41
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)


191.0703
231.0631
209.0808
245.0785
121.0284
338.3424
247.0293
326.3786
391.2849
227.0679
253.0448
413.2668
163.0751
223.0962
365.1389
387.1810
471.0744
476.4103
547.4001
561.3317
663.1761
885.3696
Intensity, cps
m/z, Da
2.0e5
1.9e5
1.8e5
1.7e5
1.6e5
1.5e5
1.4e5
1.3e5
1.2e5
1.1e5
1.0e5
9.0e4
8.0e4
7.0e4
6.0e4
5.0e4
4.0e4
3.0e4
2.0e4
1.0e4
0.0
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000

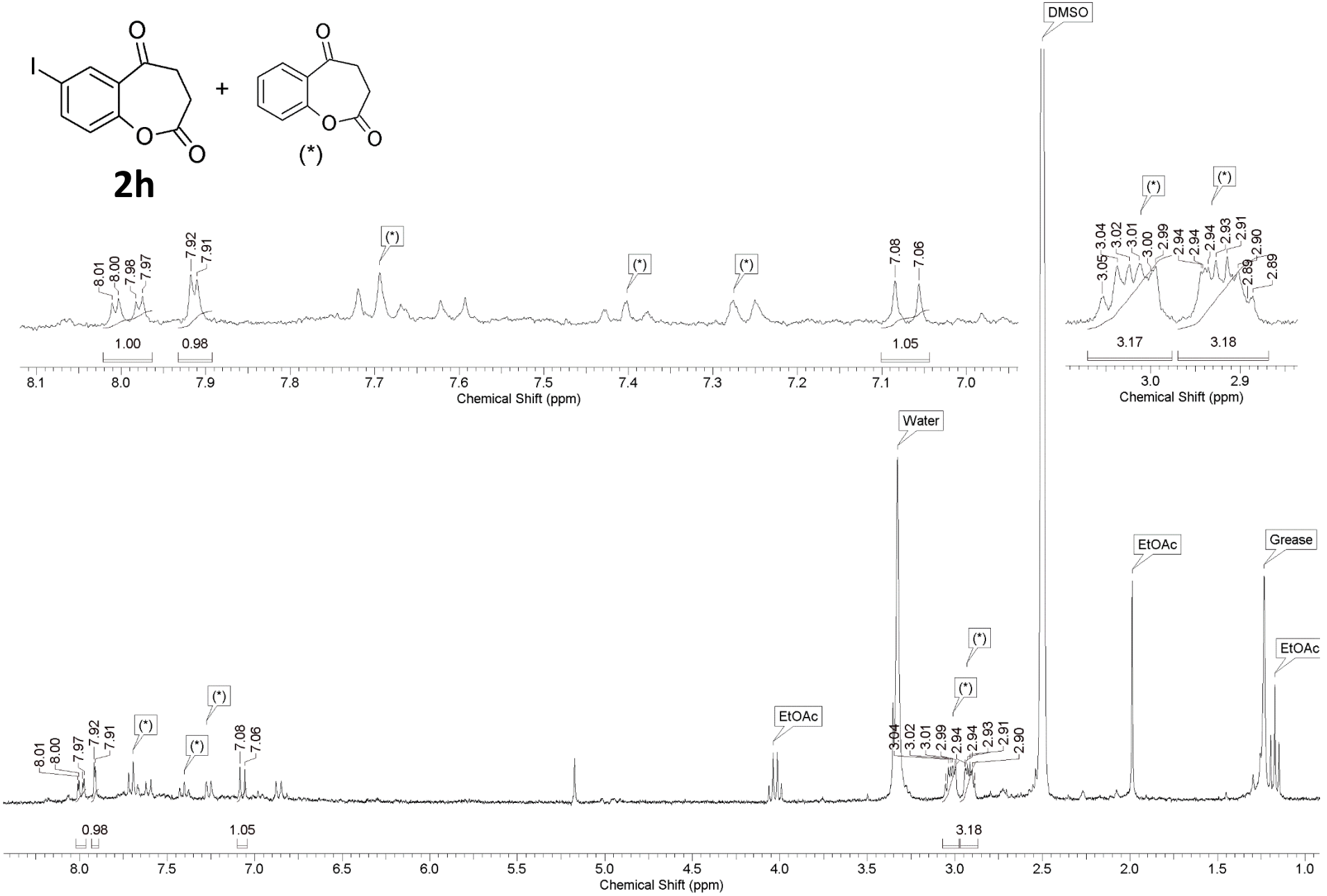
2f

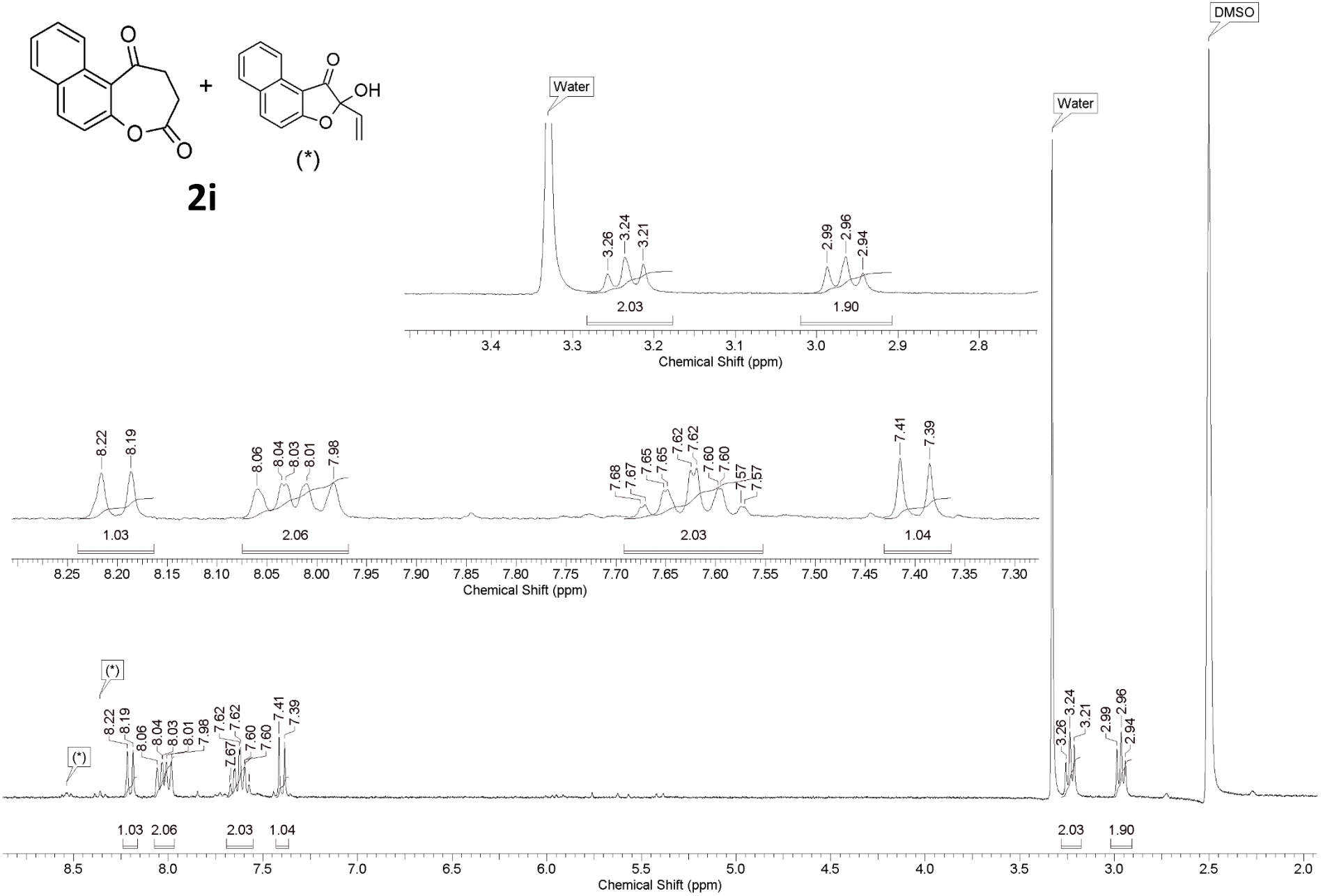

MeO2C
O
O
O
2g
Water
DMSO
3.09
3.09
3.08
3.07
3.05
3.05
2.98
2.98
2.98
2.97
2.96
2.95
2.94
2.94
2.15
2.18
3.15
3.10
3.05
3.00
2.95
2.90
2.85
Chemical Shift (ppm)
8.27
8.27
8.21
8.20
8.18
8.17
7.40
7.38
1.01
1.01
1.00
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
Chemical Shift (ppm)
3.89
3.08
3.07
3.07
3.05
3.05
2.98
2.98
2.96
2.95
1.01
1.00
3.15
2.18
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
Chemical Shift (ppm)

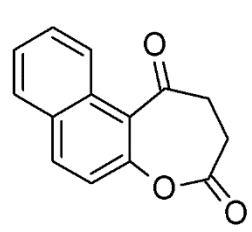

MeO2C
O
O
O

2g

DMSO
197.95
169.08
164.80
154.13
134.99
131.52
127.79
127.00
122.62
52.54
37.56
27.69
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
Chemical Shift (ppm)


2h
(*)
DMSO
Water
EtOAc
EtOAc
Grease
EtOAc
Chemical Shift (ppm)
Chemical Shift (ppm)
Chemical Shift (ppm)

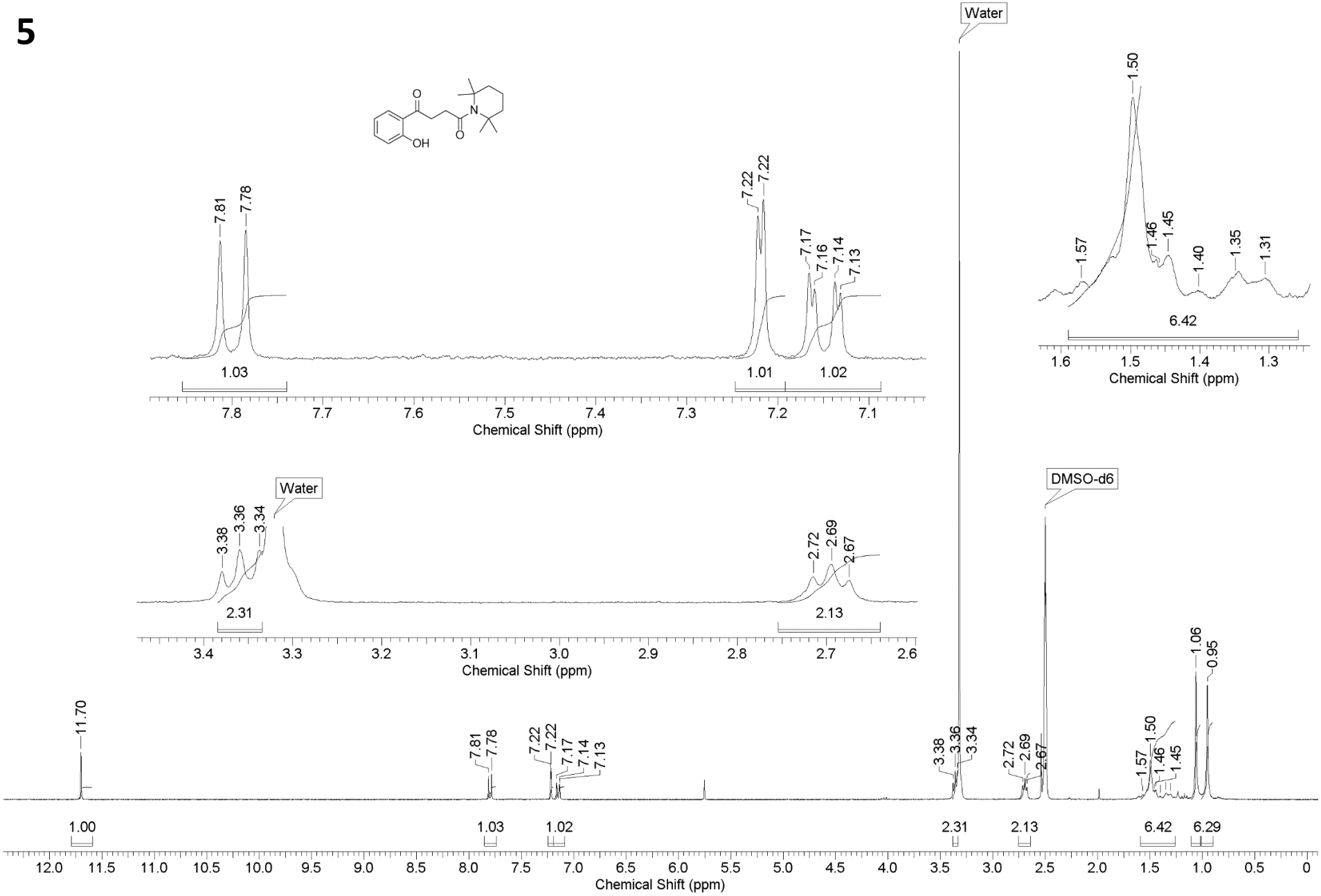

O
O
O
+
OH
O
O
(*)
2i
DMSO
Water
Water
3.26
3.24
3.21
2.99
2.96
2.94
2.03
1.90
Chemical Shift (ppm)
8.22
8.19
8.06
8.04
8.03
8.01
7.98
7.68
7.67
7.65
7.65
7.62
7.62
7.60
7.60
7.57
7.57
7.41
7.39
1.03
2.06
2.03
1.04
Chemical Shift (ppm)
(*)
(*)
1.03
2.06
2.03
1.04
2.03
1.90
Chemical Shift (ppm)



2i

DMSO
133.72
131.28
129.68
128.31
126.36
125.20
124.47
120.25
Chemical Shift (ppm)
202.48
169.85
149.44
133.72
131.28
128.31
126.36
125.20
124.47
120.25
41.62
28.26
Chemical Shift (ppm)

5


Water
DMSO-d6
11.70
7.81
7.78
7.22
7.22
7.17
7.16
7.14
7.13
3.38
3.36
3.34
2.72
2.69
2.67
1.57
1.50
1.46
1.45
1.40
1.35
1.31
1.06
0.95
1.00
1.03
1.02
2.31
2.13
6.42
6.29
Chemical Shift (ppm)

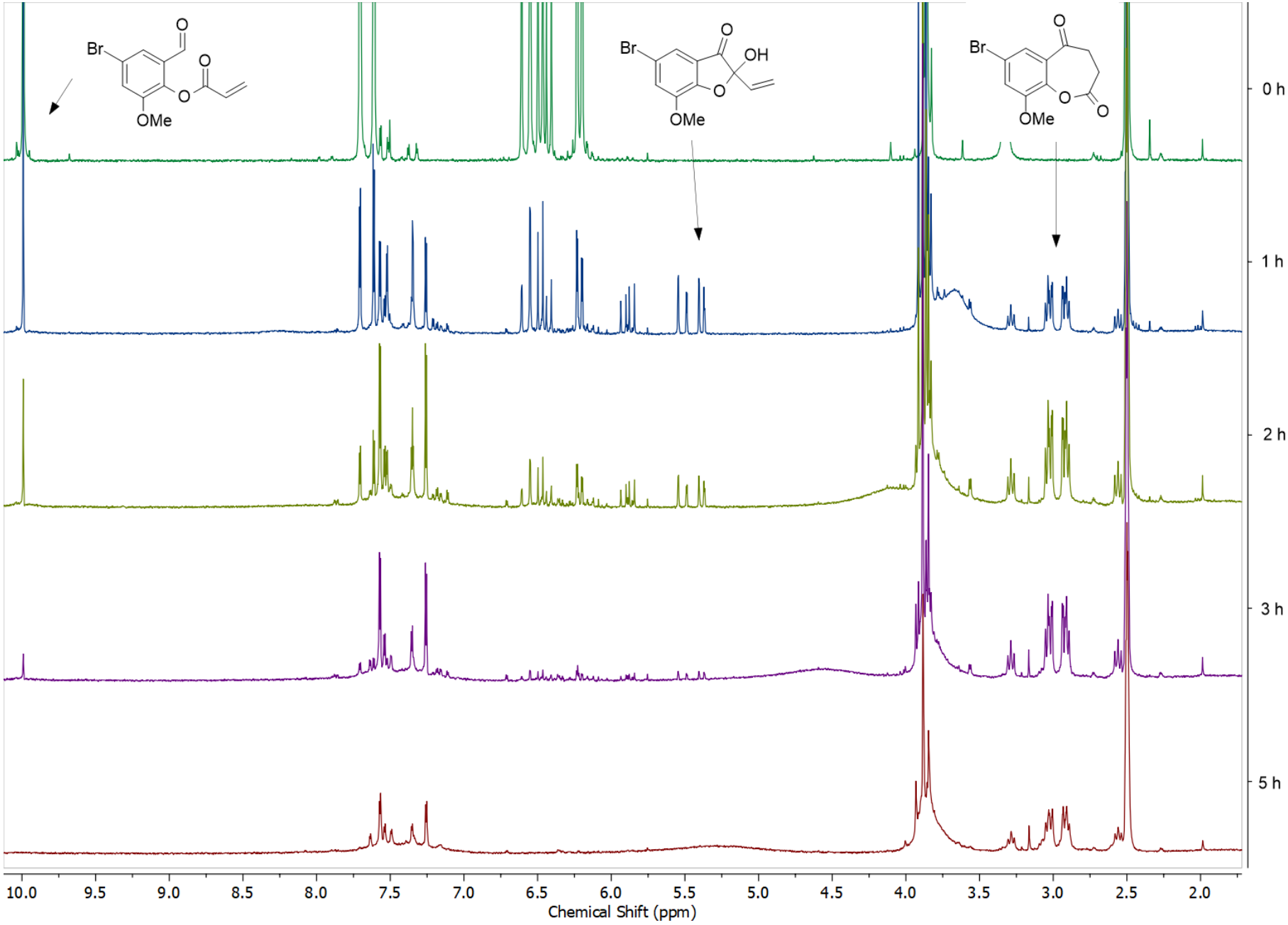
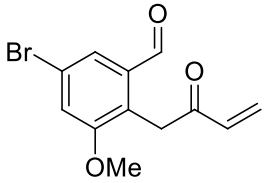
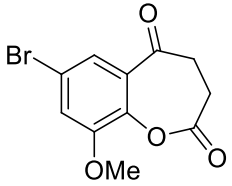
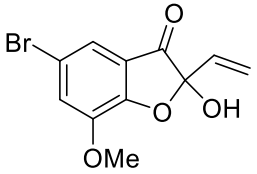

Br
O
O
O
OMe
Br
O
OH
O
OMe
Br
O
O
O
OMe
0 h
1 h
2 h
3 h
5 h
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)

Table S2. Monitoring of photochemical transformations of the substrate **1d**.

Time, hours	Mole fraction relative to the starting content of substrate **1d** in the reaction mixture, %		
	 **1d**	 **2d**	 **4**
0	100	0	0
1	36	25	19
2	10	35	8
3	3	38	4
5	0	35	0