Photochemical Reactivity of Diarylethenes: Effect of Carboxyl Group Derivatives

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I. Experimental details

General information. All commercially available reagents were used without further purification. Column chromatography was performed using silica gel 60 (0.063-0.200 mm) by Th.Geyer; TLC analysis was conducted on silica gel 60 F_{254} plates.

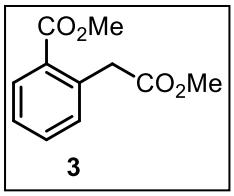
^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra were recorded on a Bruker AV400 instrument in $CDCl_3$, $(CD_3)_2SO$, and D_2O. Chemical shifts are reported in ppm using the residual signals of $CDCl_3$ $(CD_3)_2SO$, or D_2O as internal standards. Data is reported as chemical shifts (δ) in ppm, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants *J* (Hz), and integration. Mass-spectra were obtained on Shimadzu GCMS-QP5050A (70 eV) paired with a GC-17A gas chromatograph and direct sample injection into an ion source. High Resolution Mass Spectra (HRMS) were recorded using Agilent 1200/Agilent 6210 TOF HPLC and Bruker micrOTOF spectrometers equipped with an electrospray ionization source (ESI). Melting points (uncorrected) were measured on a SMP10 apparatus (Stuart).

Electronic absorption spectra were recorded with a SF-56 spectrophotometer in 1 cm quartz cuvettes. The experimental measurements were performed in solutions of dry DCM, acetonitrile, acetone and distilled H_2O in the presence of air. UV irradiation was carried out by Vilber Lourmat lamps with λ = 365 and 313 nm (15 W and 8W). The common borosilicate glass vessels and NMR tubes were used for all photolysis experiments. To prevent heating of the vessels and tubes during light irradiation, they were located 5 cm from the lamp. The light was directed from the side of the vessels and tubes.

Electron spin resonance (ESR) spectroscopy was performed at 260 K with an X-band Bruker ELEXSYS E580 ESR spectrometer equipped with ER 4131VT temperature controller and 4102ST-O-LC resonator.

I.1 Synthesis of diarylethenes

Methyl 2-(2-methoxy-2-oxoethyl)benzoate (3). To a solution of **HPA** (100 mg, 0.56 mmol) in DMF (5 mL) K_2CO_3 (77 mg, 0.56 mmol, 1 equiv.) was added. The reaction mixture was stirred for 30 min at room temperature, then CH_3I (0.04 mL, 0.56 mmol, 1 equiv.) was added and stirred for 3 days at room temperature. After reaction was completed (monitoring by NMR), the reaction mixture was poured into water (50 mL) and extracted with ethyl acetate (3 × 20 mL); the combined organic layers were washed with water, dried over anhydrous $MgSO_4$, and evaporated in vacuum. The residue was purified by column chromatography eluting by petrol. ester / ethyl acetate 8:1 to give **3**.



3

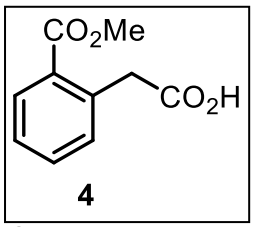
Yield 30 mg (52%), yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, J = 6.3 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.7 Hz, 1H), 7.27 (s, 1H), 4.01 (s, 2H), 3.87 (s, 3H), 3.70 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 172.1, 167.6, 136.1, 132.5, 132.4, 131.1, 129.7, 127.6, 52.1, 52.1, 40.6.

Mass spectrum, *m/z* (I_{rel}, %): 208 $[M]^+$ (0.31), 148 (100).

2-(2-(Methoxycarbonyl)phenyl)acetic acid (4). To a solution of **HPA** (5.00 g, 28 mmol) in DMF (30 mL) $NaHCO_3$ (2.25 g, 28 mmol, 1 equiv.) was added. The reaction mixture was stirred for 30 min at room temperature, then a solution of CH_3I (1.7 mL, 28 mmol, 1 equiv.) in DMF (10 mL) was added dropwise and stirred for 16 h at room temperature. After reaction was completed (monitoring by NMR), the reaction mixture was poured into water (300 mL) and extracted with ethyl acetate (3 × 80 mL); the combined organic layers were washed with water, dried over anhydrous $MgSO_4$, and evaporated in vacuum.



4

Yield 4.5 g (65%), white powder, mp 145-147 °C (lit. 146-148 °C [1]).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, J = 6.2 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 4.03 (s, 2H), 3.90 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 177.2, 167.9, 135.5, 132.7, 132.5, 131.2, 129.6, 127.8, 52.3, 40.8.

Mass spectrum, *m/z* (I_{rel}, %): 194 $[M]^+$ (0.59), 118 (100).

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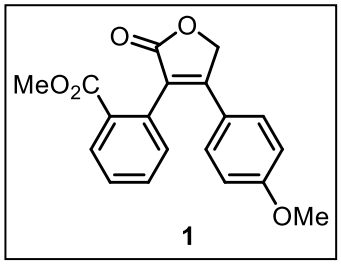
[1] K. J. McCullough, H. Tokuhara, A. Masuyama and M. Nojima, *Org. Biomol. Chem.*, 2003, **1**, 1522–1527.

Synthesis of ester diarylethenes 1 and 2. Acid **4** (1.25 g, 6.4 mmol, 1 equiv.) and K_2CO_3 (1.33 g, 9.7 mmol, 1.5 equiv.) were added in argon atmosphere into Schlenk flask, then dry DMF (25 mL) was added. The resulting suspension was stirred at room temperature for 30 min, and then bromoketone **5** (6.4 mmol, 1 equiv.) was added in argon atmosphere. The reaction mixture was stirred for 3 h at 80 ºC; after the reaction was completed (TLC control), the mixture was poured into ice water (500 mL) and extracted with ethyl acetate (4 × 50 mL); the combined organic layers were washed water (2 × 250 mL), then dried over anhydrous $MgSO_4$, and evaporated in vacuum. The residue was purified by column chromatography eluting by petrol. ester / ethyl acetate 2:1.

Methyl 2-(4-(4-methoxyphenyl)-2-oxo-2,5-dihydrofuran-3-yl)benzoate (1).



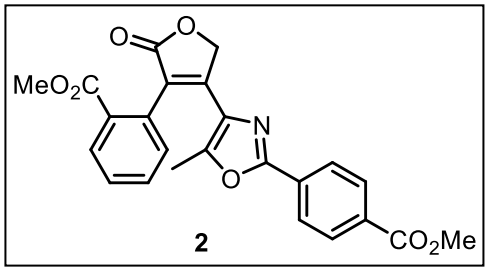
1

Yield 827 mg (40%), white powder, mp 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 7.5 Hz, 1H), 7.56 – 7.43 (m, 2H), 7.24 (d, J = 7.3 Hz, 1H), 7.15 (d, J = 8.9 Hz, 2H), 6.79 (d, J = 8.9 Hz, 2H), 5.24 (br. s, 2H), 3.79 (d, J = 7.5 Hz, 6H). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.02 (d, J = 7.7 Hz, 1H), 7.64 (t, J = 7.5 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 7.3 Hz, 1H), 7.21 (d, J = 9.1 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 5.53 (br. s, 1H), 5.30 (br. s, 1H), 3.74 (s, 3H), 3.70 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 173.4, 166.8, 161.4, 153.8, 132.8, 132.6, 131.1, 131.2, 130.8, 129.1 (2C), 128.9, 125.5, 123.0, 114.4 (2C), 70.7, 55.4, 52.3.

HRMS (ESI-TOF) *m/z*: [M+H]$^+$ Calcd for $C_{19}H_{16}O_5$: 324.1075; Found: 324.1077.

Methyl 2-(4-(2-(4-(methoxycarbonyl)phenyl)-5-methyloxazol-4-yl)-2-oxo-2,5-dihydrofuran-3-yl)benzoate (2).



2

Yield 809 mg (29%), orange powder, mp 175-177 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 – 7.99 (m, 5H), 7.54 – 7.46 (m, 2H), 7.27 (d, J = 7.5 Hz, 1H), 5.44 (s, 1H), 5.17 (s, 1H), 3.95 (s, 3H), 3.85 (s, 3H), 1.81 (s, 3H).

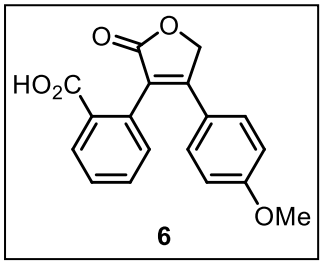
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.08 (d, J = 8.6 Hz, 2H), 8.03 – 7.91 (m, 3H), 7.69 – 7.54 (m, 2H), 7.38 (dd, J = 7.5, 1.5 Hz, 2H), 5.46 (br. s, 1H), 5.38 (br. s, 1H), 3.88 (s, 3H), 3.69 (s, 3H), 2.05 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 172.7, 167.3, 166.4, 159.8, 150.0, 147.4, 132.1, 132.1, 131.8, 131.2, 131.0, 130.7, 130.4, 130.1, 129.3, 129.0, 127.5, 126.2, 71.0, 52.4, 11.7.

HRMS (ESI-TOF) *m/z*: [M+H]$^+$ Calcd for $C_{24}H_{19}NO_7$: 433.1237; Found: 433.1239.

Synthesis of acid 6. Diarylethene **1** (200 mg, 0.6 mmol) was suspended in EtOH (2.5 mL). Solution of KOH (173 mg, 3.1 mmol, 5 equiv.) in water (2.5 mL) was added. The reaction mixture was refluxed for 10 min, then poured into water (50 mL) and washed with ethyl acetate (1 × 20 mL); then mixture was acidified with HCl_{aq} to pH = 4, extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with distilled water, dried over anhydrous $MgSO_4$, and evaporated in vacuum. The residue was treated with hexane (5 mL) and the formed precipitate was filtered off. The single crystal of **6** was obtained by slow evaporation of the mother liquor.

2-(4-(4-Methoxyphenyl)-2-oxo-2,5-dihydrofuran-3-yl)benzoic acid (6).



6

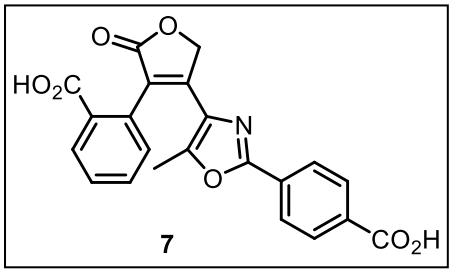
Yield 168 mg (88%), white powder, mp 114-116 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.89 (s, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.65 – 7.51 (m, 2H), 7.25 – 7.16 (m, 2H), 6.91 (d, J = 8.9 Hz, 2H), 5.56 (d, J = 17.4 Hz, 1H), 5.21 (d, J = 17.0 Hz, 1H), 3.74 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ = 172.9, 167.3, 160.9, 153.8, 132.7, 132.5, 131.6, 130.9, 130.7, 129.2 (2C), 128.8, 124.8, 122.7, 114.4 (2C), 70.5, 55.3.

HRMS (ESI-TOF) *m/z*: [M+H]$^+$ Calcd for $C_{18}H_{12}O_5$: 311.0914; Found: 311.0914.

Synthesis of acid 7. Diarylethene **2** (150 mg, 0.35 mmol) was partially dissolved in EtOH (1.4 mL). Then the solution of KOH (97 mg, 1.73 mmol, 5 equiv.) in water (1.4 mL) was added. The reaction mixture was refluxed for 10 min, then poured into water (50 mL) and washed with ethyl acetate (1 × 20 mL); then mixture was acidified with HCl to pH = 4, extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with distilled water, dried over anhydrous $MgSO_4$, and evaporated in vacuum. The residue was treated with hexane (5 mL) and the formed precipitate was filtered off.



7

2-(4-(2-(4-Carboxyphenyl)-5-methyloxazol-4-yl)-2-oxo-2,5-dihydrofuran-3-yl)benzoic acid (7).

Yield 124 mg (89%), white powder, mp 167-169 °C.

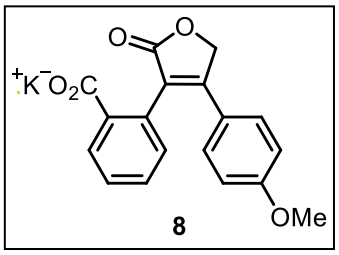
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.05 (s, 2H), 8.06 (d, J = 8.6 Hz, 2H), 8.00 (dd, J = 7.5, 1.8 Hz, 1H), 7.94 (d, J = 8.6 Hz, 2H), 7.65 – 7.52 (m, 2H), 7.32 (d, J = 7.3 Hz, 1H), 5.48 (d, J = 17.5 Hz, 1H), 5.29 (d, J = 16.7 Hz, 1H), 1.98 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ = 172.3, 167.7, 166.6, 158.7, 150.3, 146.7, 132.5, 131.9, 131.8 (2C), 131.2, 130.1, 129.5, 129.0 (2C), 128.8, 126.7, 125.9, 70.3, 11.3.

HRMS (ESI-TOF) *m/z*: [M+H]$^+$ Calcd for $C_{22}H_{15}NO_7$: 406.0921; Found: 406.0921.

Synthesis of salt 8. Diarylethene acid **6** (219 mg, 0.7 mmol) was dissolved in MeOH (3 mL), and then KOH (40 mg, 0.7 mmol, 1 equiv.) was added. The reaction mixture was stirred at room temperature for 5 min, and then solvent was evaporated in vacuum. The resulting precipitate was washed with ethyl acetate and dried in vacuum.

Potassium 2-(4-(4-methoxyphenyl)-2-oxo-2,5-dihydrofuran-3-yl)benzoate (8).



8

Yield 177 mg (72%), white powder, mp > 300 °C.

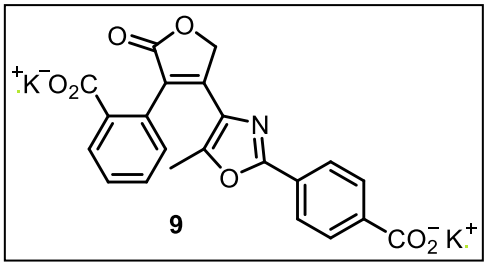
^{1}H NMR (400 MHz, D_2O): δ = 7.80 (d, J = 7.5 Hz, 1H), 7.57 – 7.44 (m, 2H), 7.26 (d, J = 8.8 Hz, 2H), 7.17 (d, J = 7.5 Hz, 1H), 6.87 (d, J = 7.9 Hz, 2H), 5.38 (d, J = 14.2 Hz, 2H), 3.79 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, D_2O): δ = 177.3, 175.2, 160.9, 156.7, 138.7, 130.3, 130.2, 129.5 (2C), 129.4, 129.2, 128.9, 124.4, 122.9, 114.3 (2C), 72.0, 55.3.

HRMS (ESI-TOF) *m/z*: $[M-K+2H]^+$ Calcd for $C_{18}H_{13}KO_5$: 311.0914; Found: 311.0916.

Synthesis of salt 9. Diarylethene acid **7** (84 mg, 0.2 mmol) was suspended in MeOH (3 mL), and then KOH (21 mg, 0.4 mmol, 2 equiv.) was added. The reaction mixture was stirred at room temperature for 5 min, and then solvent was evaporated in vacuum. The resulting precipitate was washed with ethyl acetate and dried in vacuum.

Potassium 2-(4-(2-(4-carboxylatophenyl)-5-methyloxazol-4-yl)-2-oxo-2,5-dihydrofuran-3-yl)benzoate (9).



9

Yield 91 mg (91%), white powder, mp > 300 °C.

^{1}H NMR (400 MHz, D_2O): δ = 7.91 (s, 4H), 7.79 (d, J = 6.9 Hz, 1H), 7.56 – 7.45 (m, 2H), 7.29 (d, J = 6.7 Hz, 1H), 5.36 (d, J = 15.6 Hz, 2H), 1.88 (s, 3H).

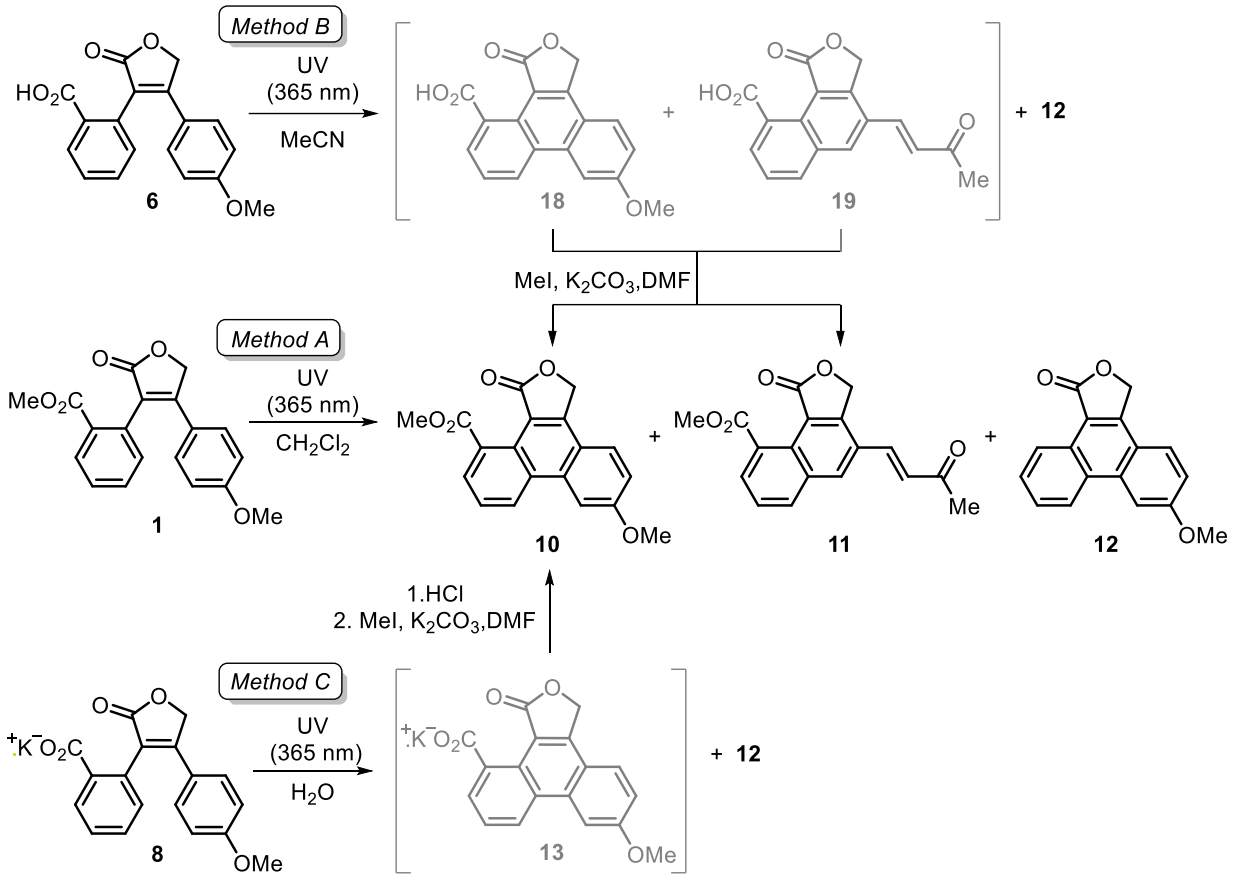
^{13}C{^{1}H} NMR (101 MHz, D_2O): δ = 176.2, 175.3, 174.6, 160.6, 151.3, 148.8, 138.7, 138.5, 130.6, 129.9, 129.3 (2C), 129.1 (2C), 128.9, 127.9, 127.8, 127.0, 126.0 (2C), 71.8, 10.8.

HRMS (ESI-TOF) *m/z*: $[M-2K+3H]^+$ Calcd for $C_{22}H_{13}K_2NO_7$: 406.0921; Found: 406.0929.

II.2 Photochemical reactions of diarylethenes

Synthesis of photoproducts 10, 11, 12.

Scheme S1. Synthetic routes to photoproducts **10**, **11**, **12**.



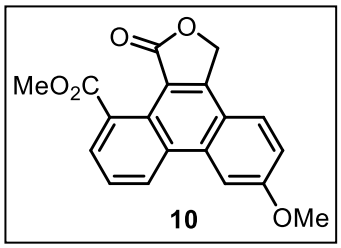
Method A. Diarylethene **1** (65 mg, 0.2 mmol) was dissolved in anhydrous dichloromethane (50 mL). The reaction mixture was irradiated with UV light (365 nm, 15 W) for 27 h, then products were separated by column chromatography eluting by petroleum ester / ethyl acetate 3:1 and purified by recrystallization from hexane.

Method B. Diarylethene acid **6** (100 mg, 0.3 mmol) was dissolved in anhydrous acetonitrile (50 mL). The reaction mixture was irradiated with UV light (365 nm, 15 W) for 23 h, then solvent was evaporated in vacuum. To obtained dry reaction mixture K_2CO_3 (222 mg, 1.6 mmol, 5 equiv.) in DMF (2 mL) was added, reaction mixture was stirred at room temperature for 5 min, then MeI (0.04 mL, 0.7 mmol, 2 equiv.) was added. The reaction mixture was stirred further for 10 min, poured into water (50 mL), extracted with ethyl acetate (3 × 20 mL), washed with water (1 × 50 mL), dried over anhydrous $MgSO_4$, and evaporated in vacuum. The alkylated products were separated by column chromatography eluting by petroleum ester / ethyl acetate 3:1 and purified by recrystallization from hexane.

Method C. Diarylethene salt **8** (85 mg, 0.3 mmol) was dissolved in distilled water (35 mL). The reaction mixture was irradiated with UV light (365 nm, 15 W) for 10 h, then HCl was

added to pH = 4, extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with distilled water, dried over anhydrous $MgSO_4$, and evaporated in vacuum. The residue was dissolved in DMF (2 mL) and K_2CO_3 (169 mg, 1.2 mmol, 5 equiv.) was added, reaction mixture was stirred at room temperature for 5 min, then MeI (0.03 mL, 0.5 mmol, 2 equiv.) was added. The reaction mixture was stirred further for 10 min, poured into water (50 mL), extracted with ethyl acetate (3 × 20 mL), washed with water (50 mL), dried over anhydrous $MgSO_4$, and evaporated in vacuum. The residue was purified by column chromatography eluting by petroleum ester / ethyl acetate 5:1.

Methyl 9-methoxy-3-oxo-1,3-dihydrophenanthro[9,10-*c*]furan-4-carboxylate (10).



10

Method A: yield 25 mg (39%), *method B:* yield 5 mg (5%), *method C:* yield 10 mg (12%), white powder, mp 220-222 °C.

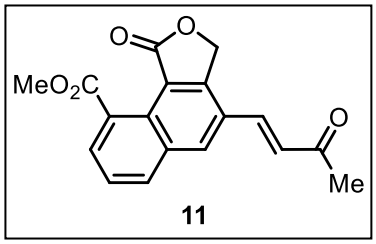
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.09 (d, J = 8.3 Hz, 1H), 8.29 (s, 1H), 7.99 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 7.2 Hz, 1H), 7.79 (t, J = 7.8 Hz, 1H), 7.44 (d, J = 8.8 Hz, 1H), 5.76 (s, 1H), 4.05 (s, 1H), 3.82 (s, 1H).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (d, J = 8.6 Hz, 1H), 8.05 (s, 1H), 7.95 (d, J = 8.5 Hz, 1H), 7.80 – 7.68 (m, 2H), 7.35 (dd, J = 8.8, 2.5 Hz, 1H), 5.58 (s, 2H), 4.07 (s, 3H), 3.99 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ = 170.4, 168.9, 161.5, 151.7, 134.3, 130.6, 130.1, 129.1, 127.0, 126.9, 126.6, 122.6, 119.2, 118.4, 115.1, 105.9, 68.5, 55.9, 52.0.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{14}O_5$ ($[M]^+$): 323.0914; Found: 323.0914.

(*E*)-Methyl 1-oxo-4-(3-oxobut-1-en-1-yl)-1,3-dihydronaphtho[1,2-*c*]furan-9-carboxylate (11).



11

Method A: yield 18 mg (29%), *method B:* yield 12 mg (12%).

Yellow amorphous powder.

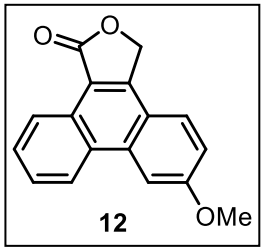
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 1H), 8.09 (d, J = 7.0 Hz, 1H), 7.96 (d, J = 7.9 Hz, 1H), 7.72 – 7.55 (m, 2H), 6.71 (d, J = 16.4 Hz, 1H), 5.51 (s, 2H), 3.98 (s, 3H), 2.46 (s, 3H).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.84 (s, 1H), 8.32 (d, J = 7.5 Hz, 1H), 7.93 (d, J = 6.0 Hz, 1H), 7.77 (t, J = 7.7 Hz, 1H), 7.71 (d, J = 16.5 Hz, 1H), 6.91 (d, J = 16.4 Hz, 1H), 5.77 (s, 2H), 3.82 (s, 3H), 2.42 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ = 197.9, 169.5, 168.5, 150.1, 137.3, 135.5, 133.7, 132.5, 130.9, 130.5, 129.4, 127.7, 126.9, 124.4, 119.9, 69.1, 52.1, 27.8.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{14}O_5$ ($[M]^+$): 311.0914; Found: 311.0914.

6-Methoxyphenanthro[9,10-*c*]furan-1(3*H*)-one (12).



Method A: yield 8 mg (15%), *method B:* yield 3 mg (4%), *method C:* yield 17 mg (22%), white powder, mp 186-188°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.13 – 9.06 (m, 1H), 8.63 (d, J = 7.1 Hz, 1H), 8.12 (s, 1H), 7.82 – 7.70 (m, 3H), 7.34 (dd, J = 8.8, 2.6 Hz, 1H), 5.61 (s, 2H), 4.08 (s, 3H).

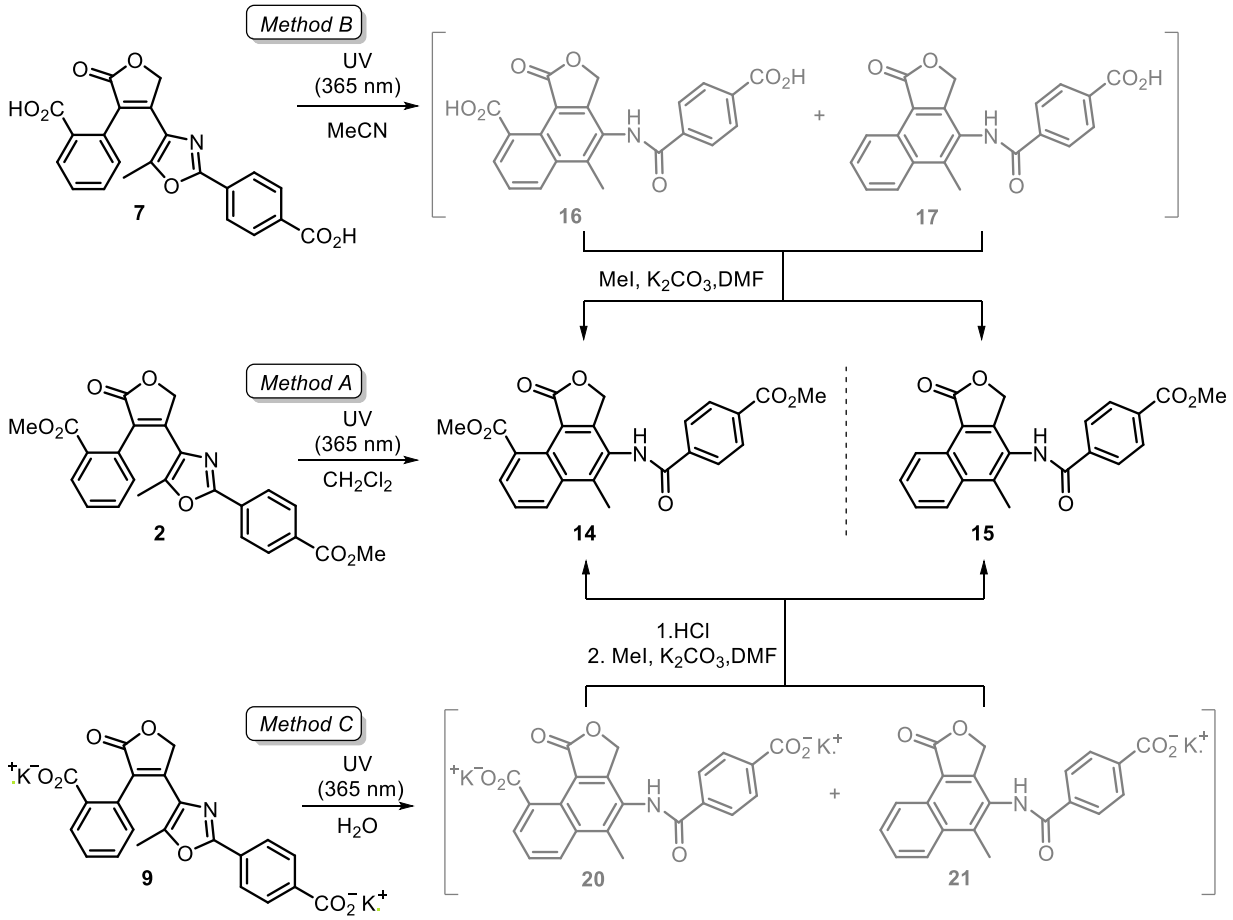
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.99 – 8.85 (m, 2H), 8.32 (d, J = 2.5 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.79 (tt, J = 7.2, 5.3 Hz, 2H), 7.44 (dd, J = 8.8, 2.4 Hz, 1H), 5.77 (s, 2H), 4.06 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 171.5, 161.2, 150.3, 134.6, 129.6, 128.4, 127.3, 127.1, 126.4, 124.3, 122.9, 119.2, 117.8, 115.0, 105.7, 68.6, 55.8.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{12}O_3$ ($[M]^+$): 265.0859; Found: 265.0859.

Synthesis of photoproducts 14, 15.

Scheme S2. Synthetic routes to photoproducts **14**, **15**.



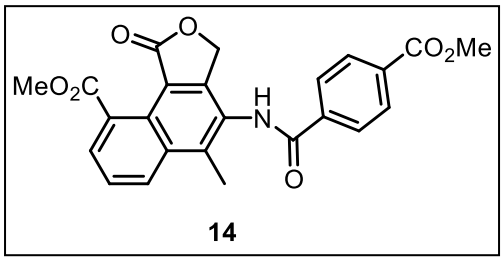
Method A. Diarylethene **2** (75 mg, 0.2 mmol) was dissolved in anhydrous dichloromethane (50 mL). The reaction mixture was irradiated with UV light (365 nm, 15 W) for 6 h. After the reaction was completed (TLC control), the solvent was removed in vacuum and the residue was purified by column chromatography eluting by petroleum ester / ethyl acetate 1:1.

Method B. Diarylethene acid **7** (70 mg, 0.2 mmol) was dissolved in anhydrous acetonitrile (50 mL). The reaction mixture was irradiated with UV light (365 nm, 15 W) for 13 h, then solvent was evaporated in vacuum. To obtained dry reaction mixture K_2CO_3 (119 mg, 0.9 mmol, 5 equiv.) in DMF (2 mL) was added, reaction mixture was stirred at room temperature for 5 min, then MeI (0.04 mL, 0.7 mmol, 4 equiv.) was added. The reaction mixture was stirred for 10 min, poured into water (50 mL), extracted with ethyl acetate (3 × 20 mL), washed with water (1 × 50 mL), dried over anhydrous $MgSO_4$, and evaporated in vacuum. The alkylated products were separated by column chromatography eluting by petroleum ester / ethyl acetate 2:1.

Method C. Diarylethene salt **9** (170 mg, 0.4 mmol) was dissolved in distilled water (50 mL). The reaction mixture was irradiated with UV light (365 nm, 15 W) for 6 h, then HCl was added to pH = 4, extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with distilled water, dried over anhydrous $MgSO_4$, and evaporated in vacuum. To

obtained dry reaction mixture K_2CO_3 (294 mg, 2.1 mmol, 5 equiv.) in DMF (2 mL) was added, reaction mixture was stirred at room temperature for 5 min, then MeI (0.1 mL, 1.7 mmol, 4 equiv.) was added. The reaction mixture was stirred further for 10 min, poured into water (50 mL), extracted with ethyl acetate (3 × 20 mL), washed with water (1 × 50 mL), dried over anhydrous $MgSO_4$, and evaporated in vacuum. The alkylated products were separated by column chromatography eluting by petroleum ester / ethyl acetate 2:1.

Methyl 4-(4-(methoxycarbonyl)benzamido)-5-methyl-1-oxo-1,3-dihydronaphtho [1,2-*c*]furan-9-carboxylate (14).



14

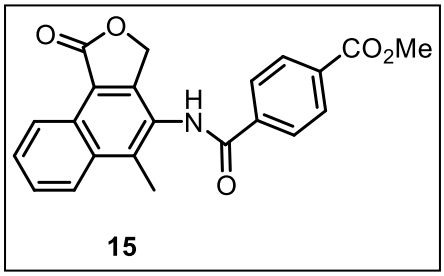
Method A: yield 61 mg (81%), *method B:* yield 14 mg (19%), *method C:* yield 25 mg (16%), white powder, mp 285-287°C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.73 (s, 1H), 8.49 (d, J = 8.5 Hz, 1H), 8.17 (q, J = 8.6 Hz, 4H), 7.94 (d, J = 7.2 Hz, 1H), 7.81 (t, J = 7.8 Hz, 1H), 5.44 (s, 2H), 3.92 (s, 3H), 3.82 (s, 3H), 2.73 (s, 3H).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.10 (s, 1H), 8.27 – 8.22 (m, 4H), 8.03 (d, J = 8.6 Hz, 1H), 7.68 (d, J = 7.0 Hz, 1H), 7.55 (d, J = 7.2 Hz, 1H), 4.64 (br. s, 2H), 4.00 (d, J = 6.6 Hz, 6H), 2.57 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ = 169.6, 168.7, 165.6, 165.1, 149.2, 139.2, 137.6, 133.7, 132.5, 129.8, 129.5, 129.3 (2C), 128.7, 128.5, 128.3 (2C), 126.6, 123.2, 118.1, 68.3, 52.5, 52.1, 14.8. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{19}NO_7$ ($[M]^+$): 434.1234; Found: 433.1234.

Methyl 4-((5-methyl-1-oxo-1,3-dihydronaphtho[1,2-*c*]furan-4-yl)carbamoyl)benzoate (15).



15

Method B: yield 4 mg (6%), *method C:* yield 42 mg (32%), white powder, mp 151-153°C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.66 (s, 1H), 8.90 (d, J = 8.0 Hz, 1H), 8.32 (d, J = 9.1 Hz, 1H), 8.17 (q, J = 8.6 Hz, 4H), 7.87 – 7.73 (m, 2H), 5.42 (s, 2H), 3.92 (s, 3H), 2.70 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ = 170.8, 165.7, 164.9, 147.8, 138.9, 137.8, 132.9, 132.4, 129.3 (2C), 128.5, 128.3 (2C), 127.7, 127.5, 127.3, 125.8, 122.5, 117.6, 68.5, 52.5, 14.5.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{17}NO_5$ ($[M]^+$): 376.1180; Found: 376.1182.

II. NMR studies

II.1 NMR monitoring of photochemical reactions

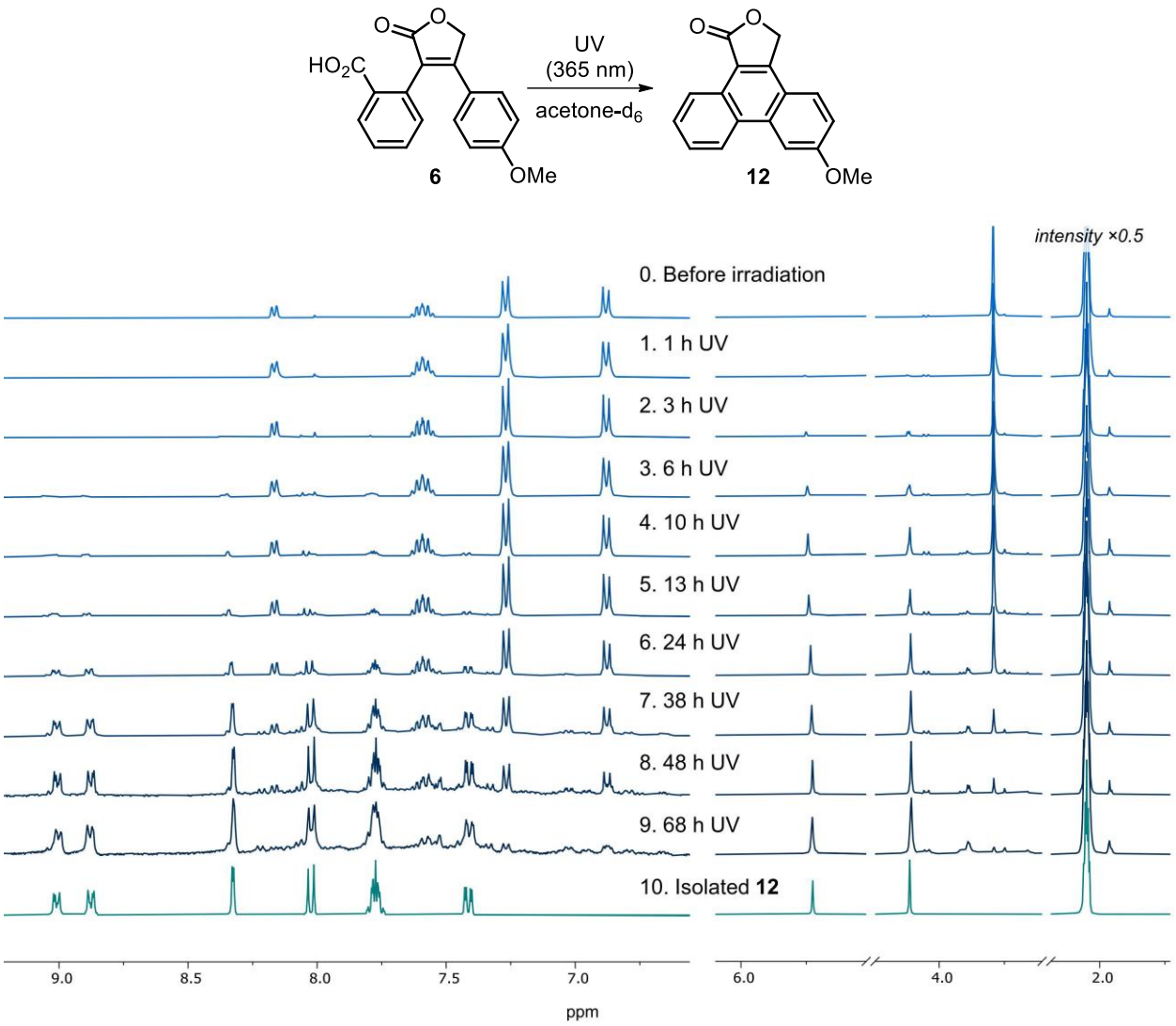


Figure S1. ^{1}H NMR monitoring of **6** irradiated by UV light (365 nm) in acetone-d_6 over 68 h from top to bottom.

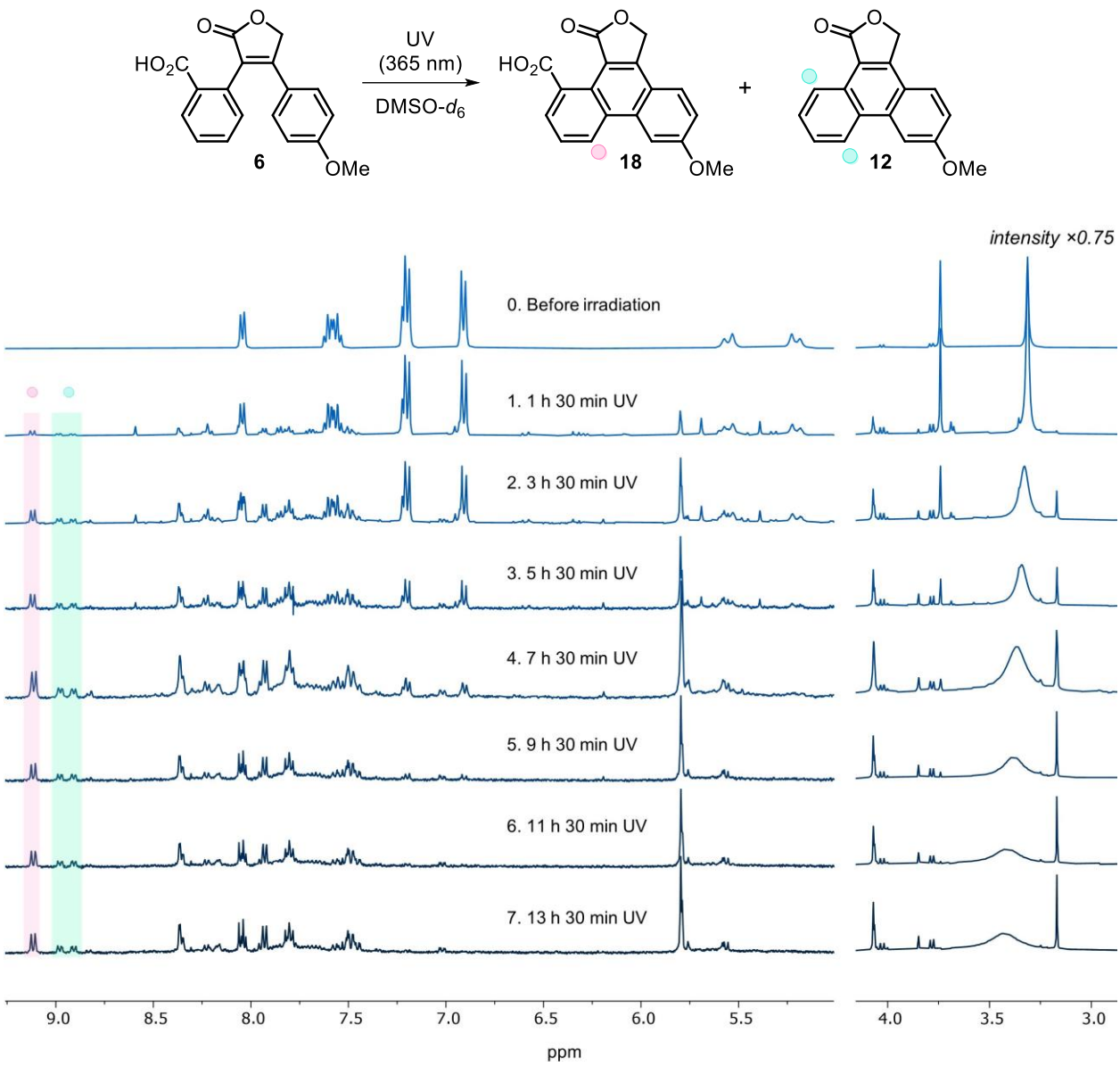


Figure S2. ^{1}H NMR monitoring of **6** irradiated by UV light (365 nm) in DMSO-d_6 over 13 h 30 min from top to bottom.

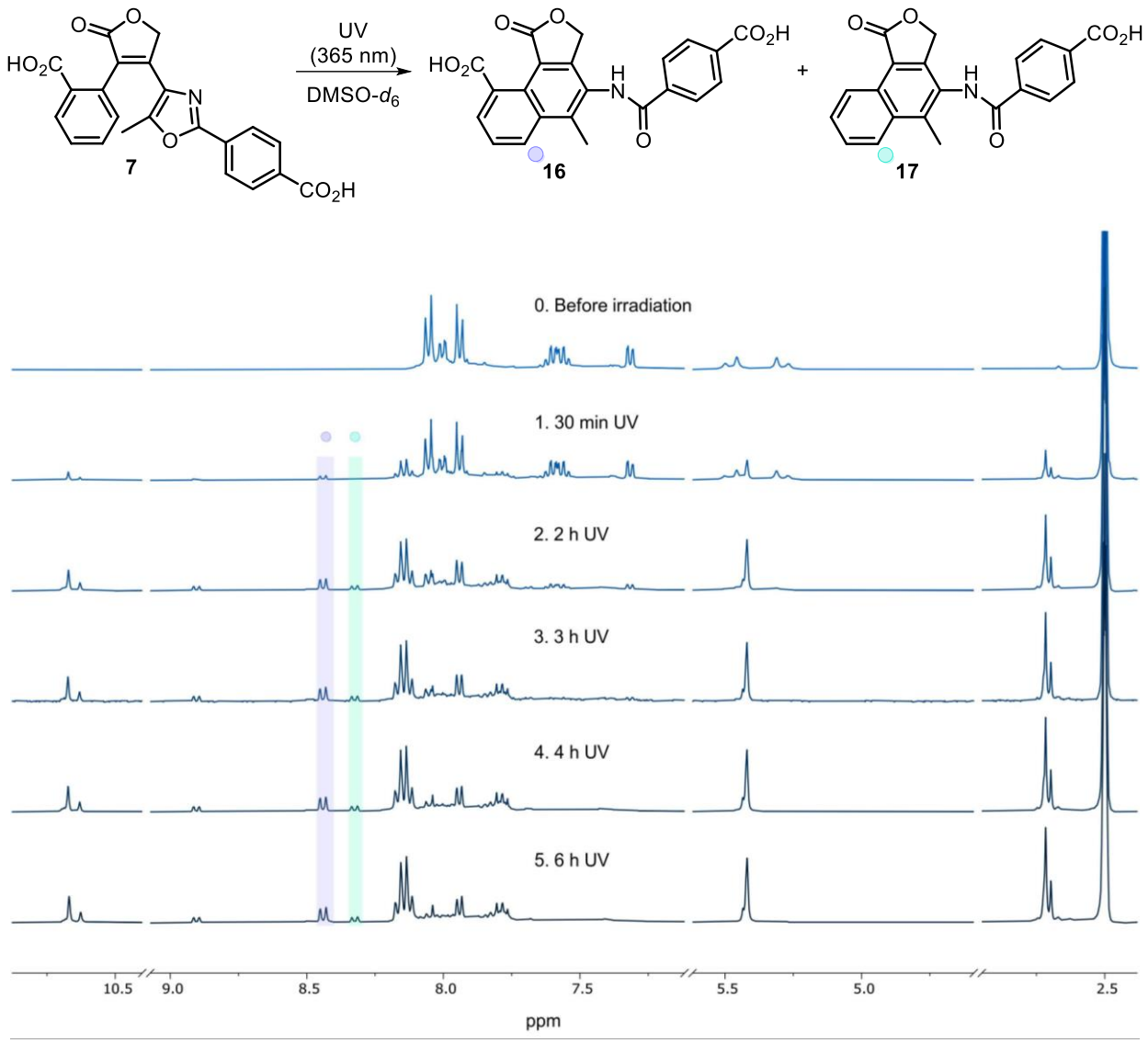


Figure S3. ^{1}H NMR monitoring of **7** irradiated by UV light (365 nm) in DMSO-d_6 over 6 h from top to bottom.

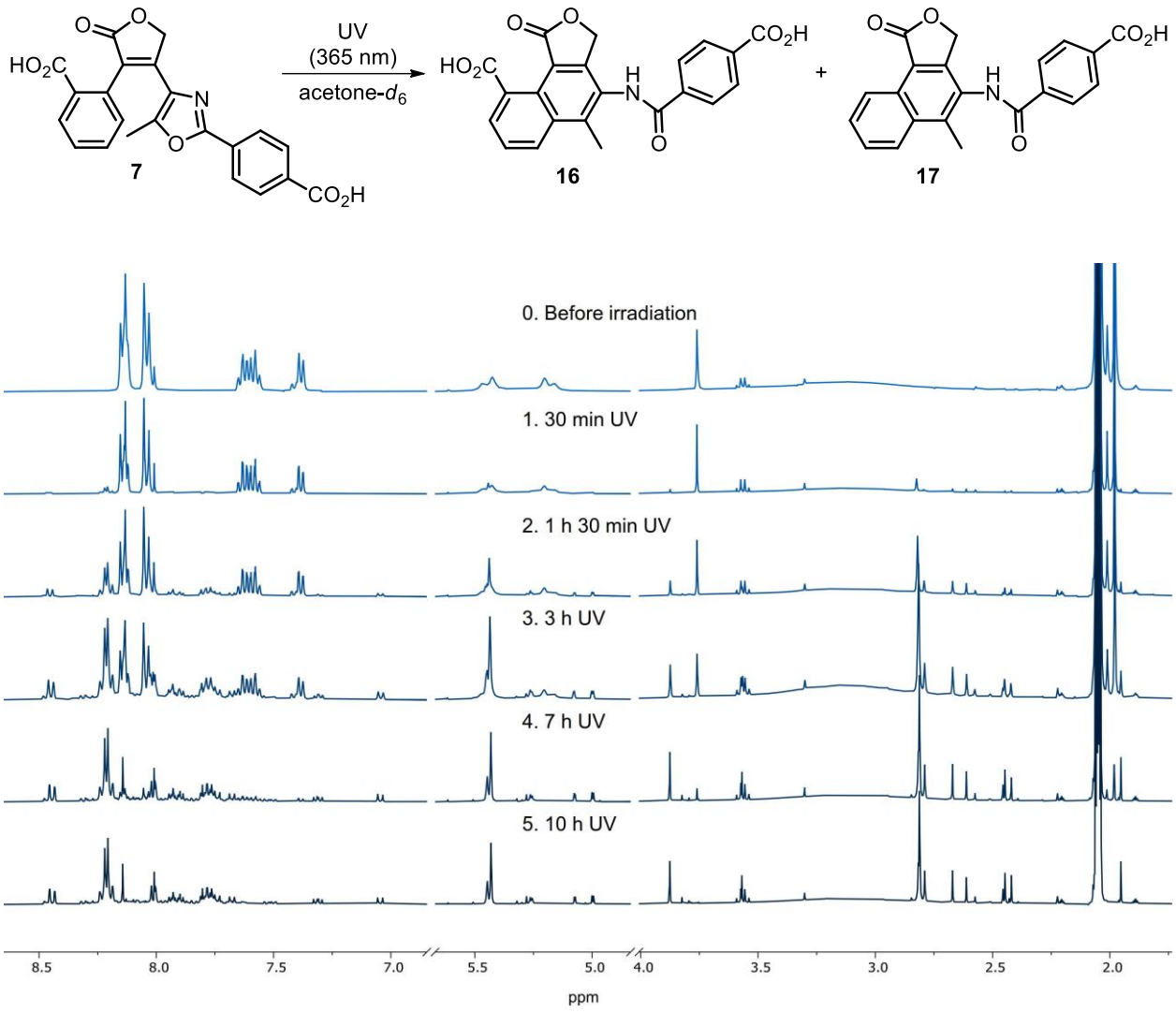


Figure S4. ^{1}H NMR monitoring of **7** irradiated by UV light (365 nm) in acetone-d_6 over 10 h from top to bottom.

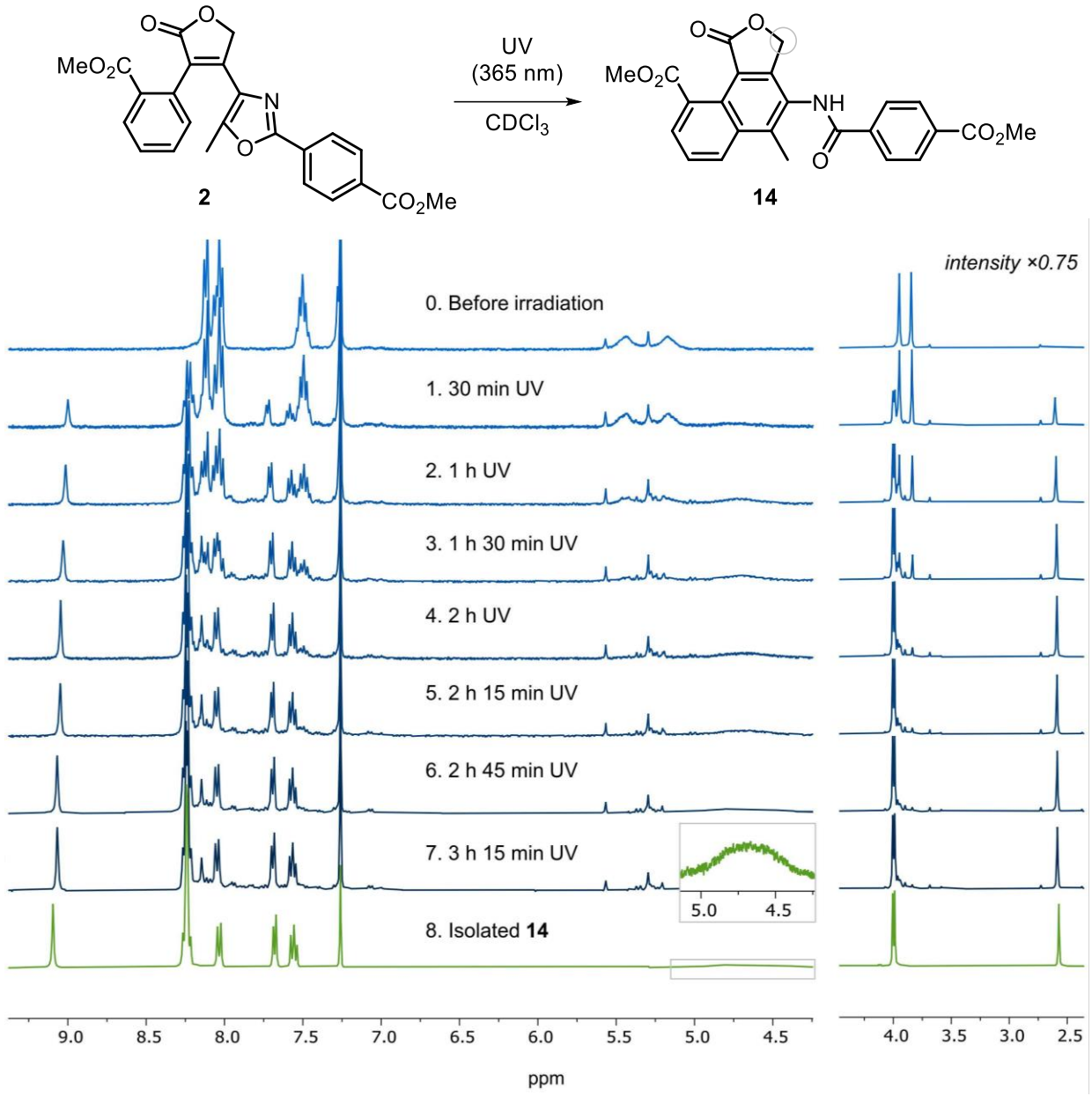


Figure S5. ^{1}H NMR monitoring of **2** irradiated by UV light (365 nm) in $CDCl_3$ over 3 h 15 min from top to bottom and the spectra of **14** for comparison. The broad signal of methylene protons is framed.

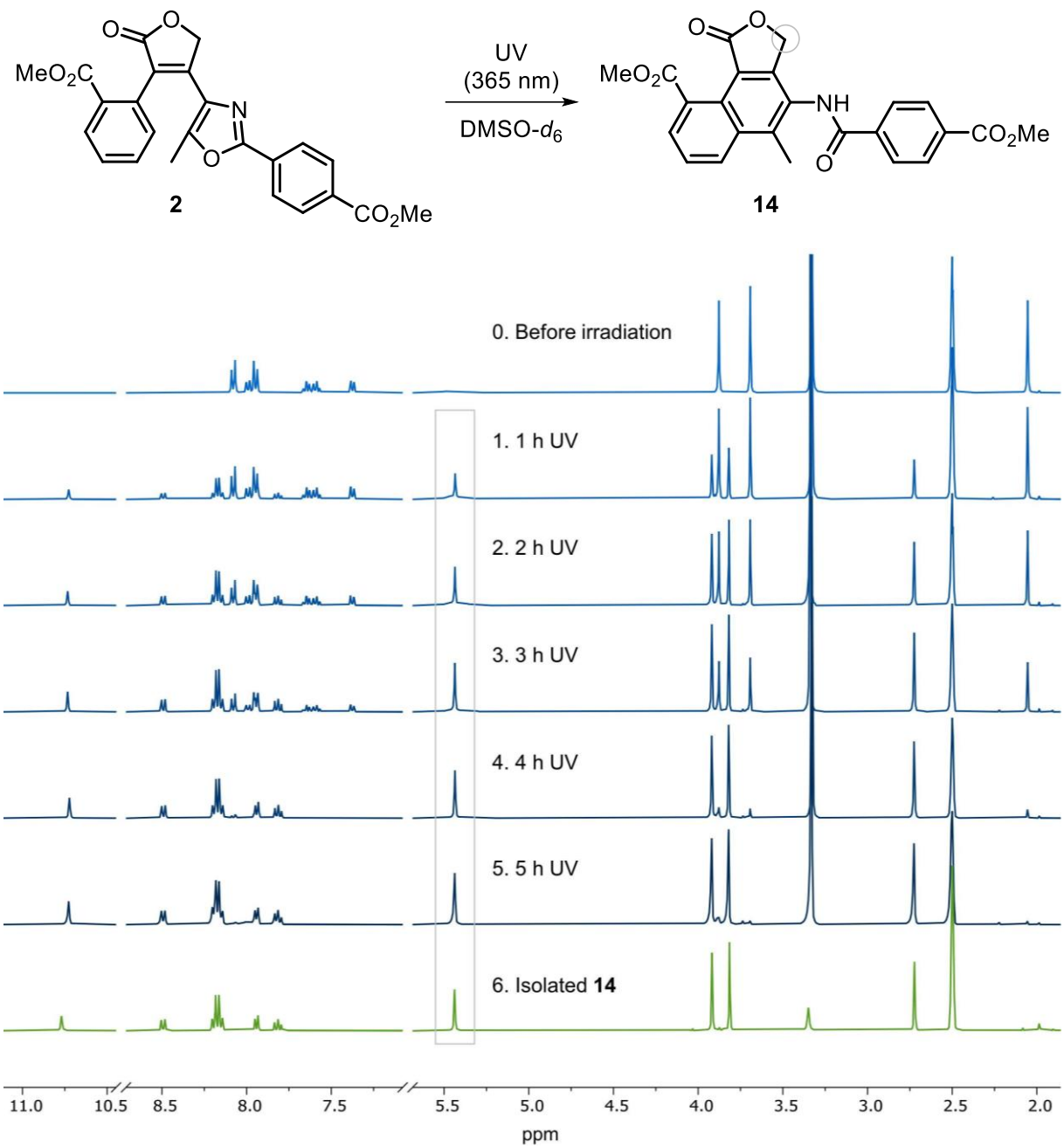


Figure S6. ^{1}H NMR monitoring of **2** irradiated by UV light (365 nm) in DMSO-d_6 over 5 h from top to bottom and the spectra of **14** for comparison. The signal of methylene protons is framed.

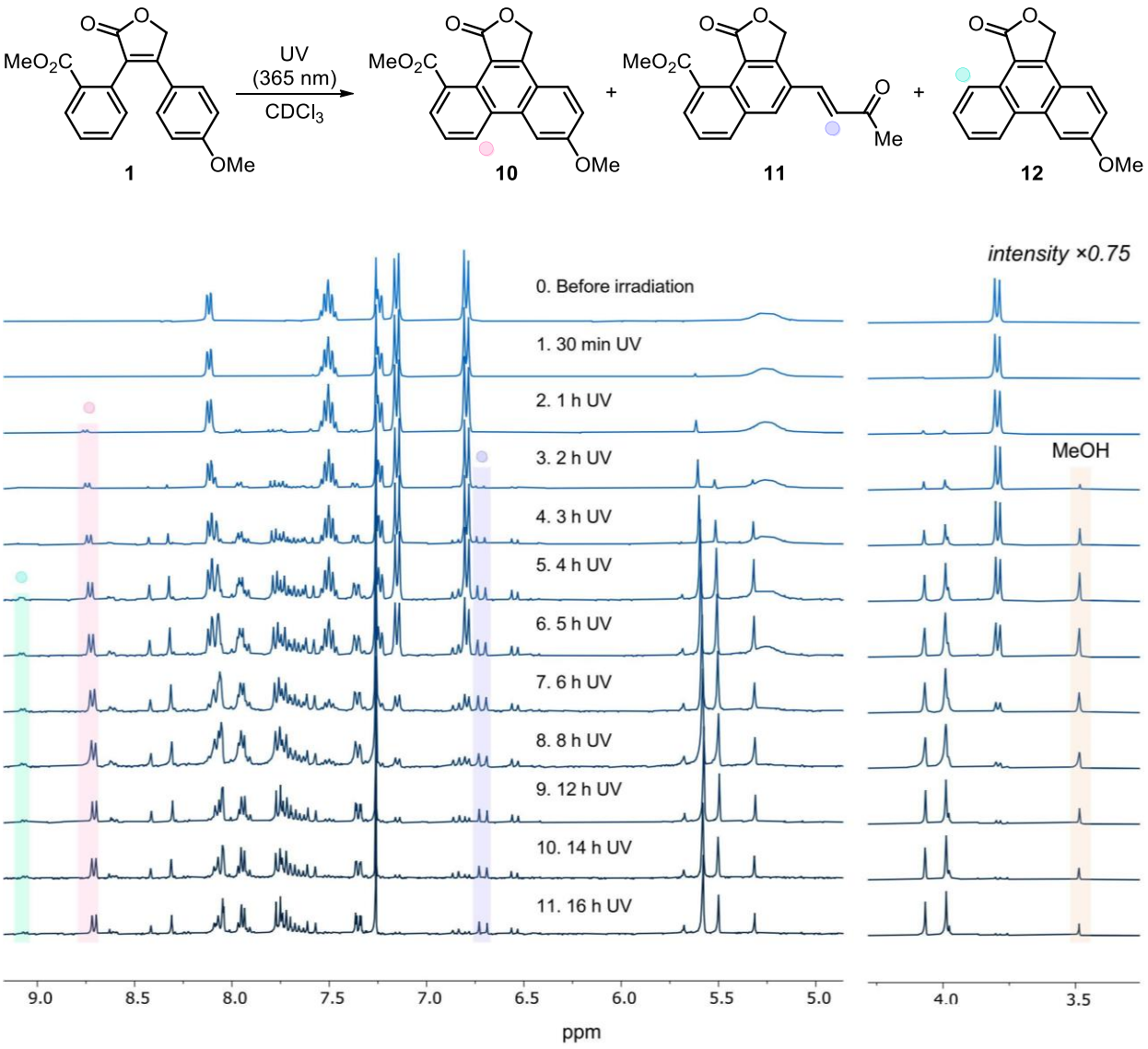


Figure S7. ^{1}H NMR monitoring of **1** irradiated by UV light (365 nm) in $CDCl_3$ over 16 h from top to bottom.

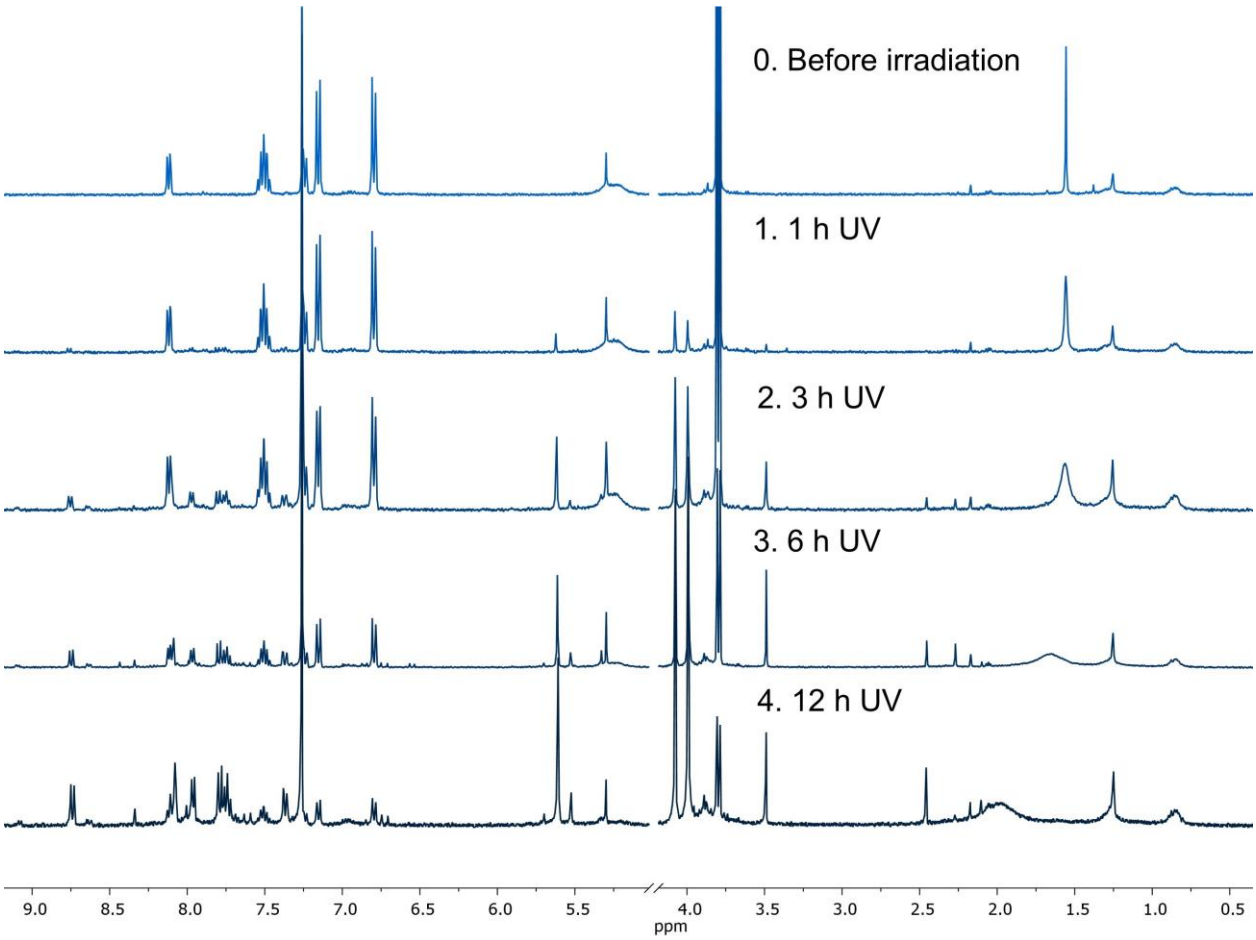


Figure S8. ^{1}H NMR monitoring of **1** irradiated by UV light (365 nm) in $CDCl_3$ over 12 h from top to bottom. The photolysis was performed in inert atmosphere.

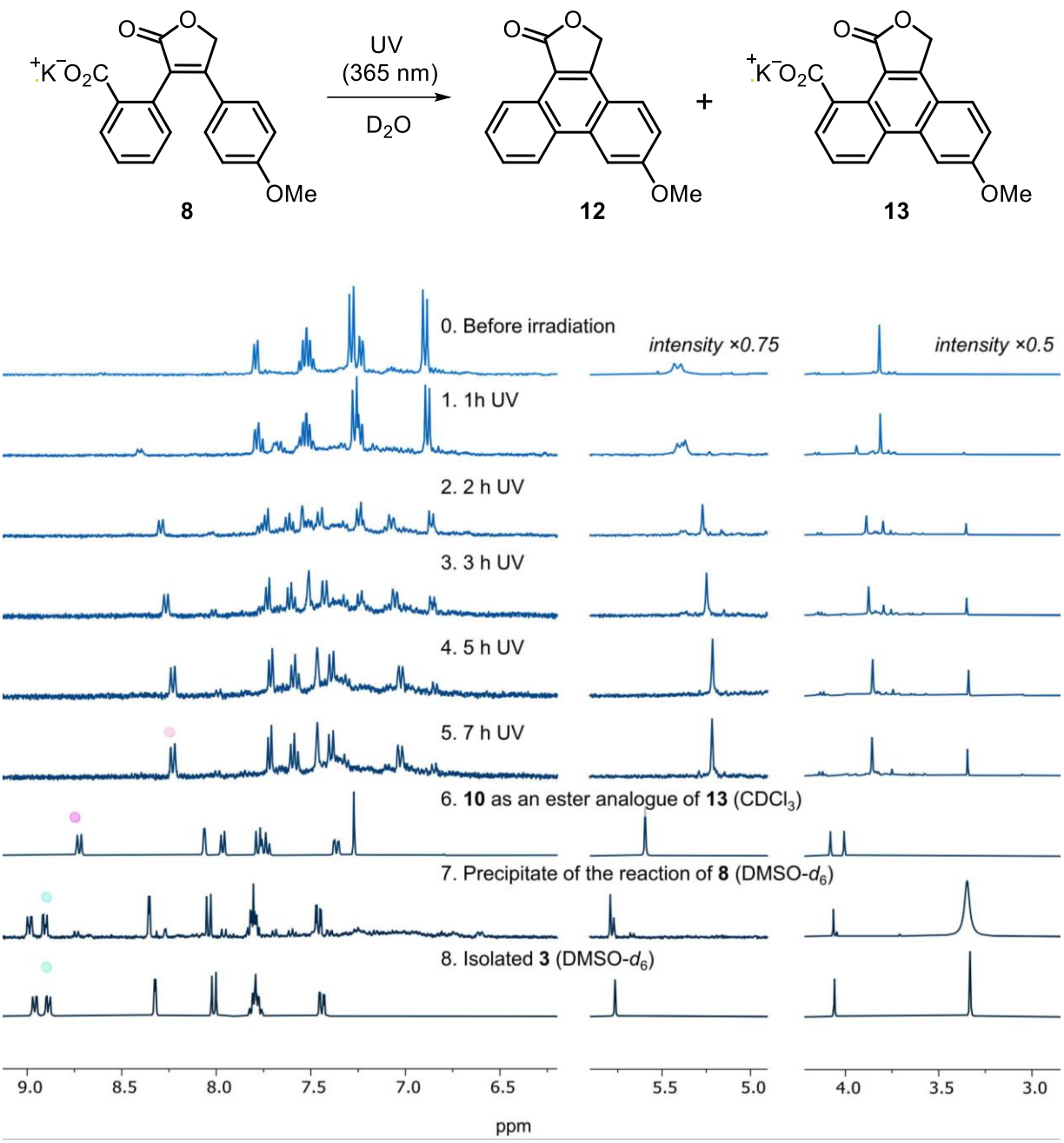


Figure S9. ^{1}H NMR monitoring of **8** irradiated by UV light (365 nm) in D_2O over 7 h from top to bottom, showing formation of single **13**, spectrum of filtered precipitation of the reaction in DMSO-d_6 and the spectrum of **12** in DMSO-d_6 for comparison (both pink).

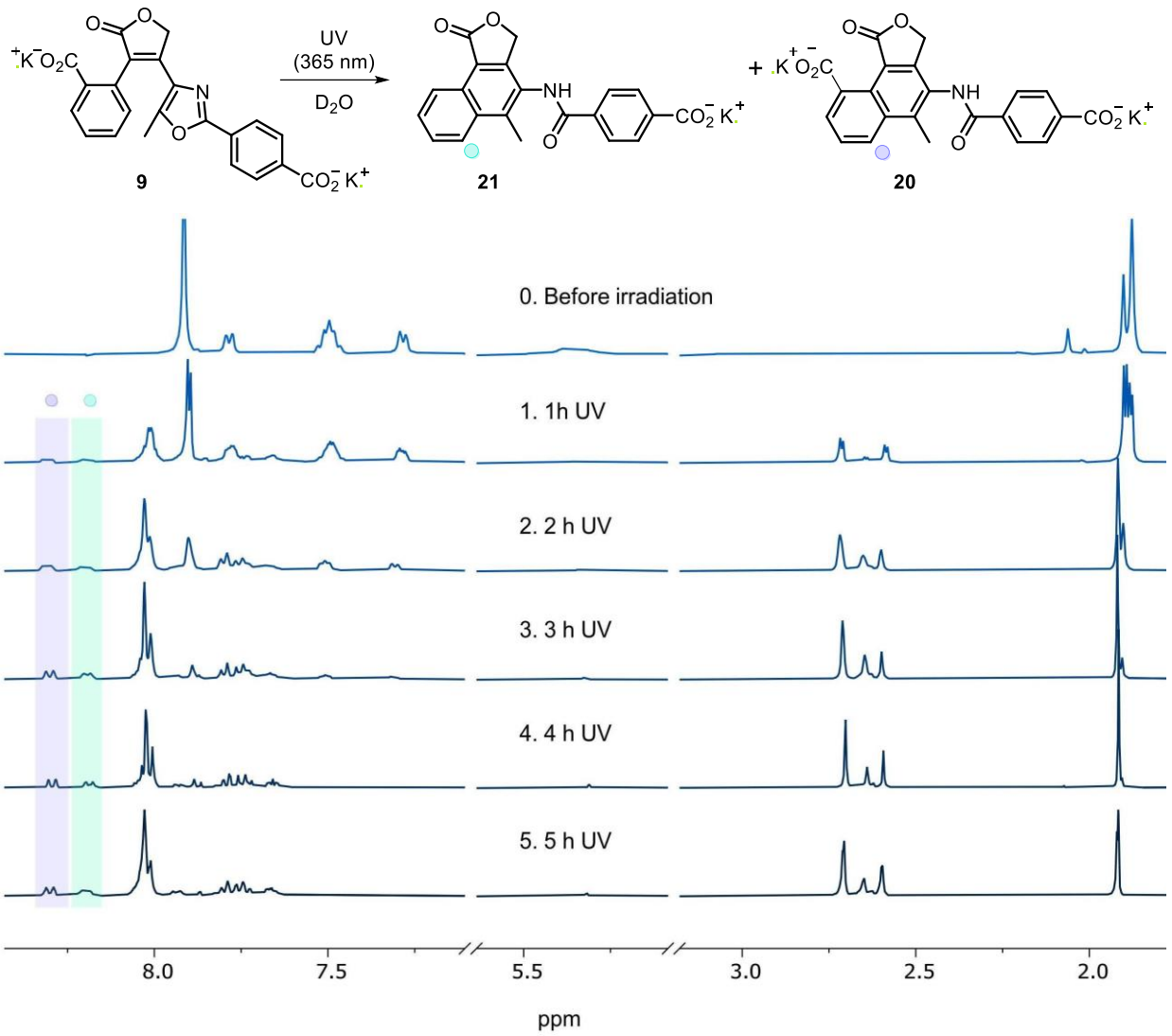


Figure S10. ^{1}H NMR monitoring of **9** irradiated by UV light (365 nm) in D_2O over 5 h from top to bottom.

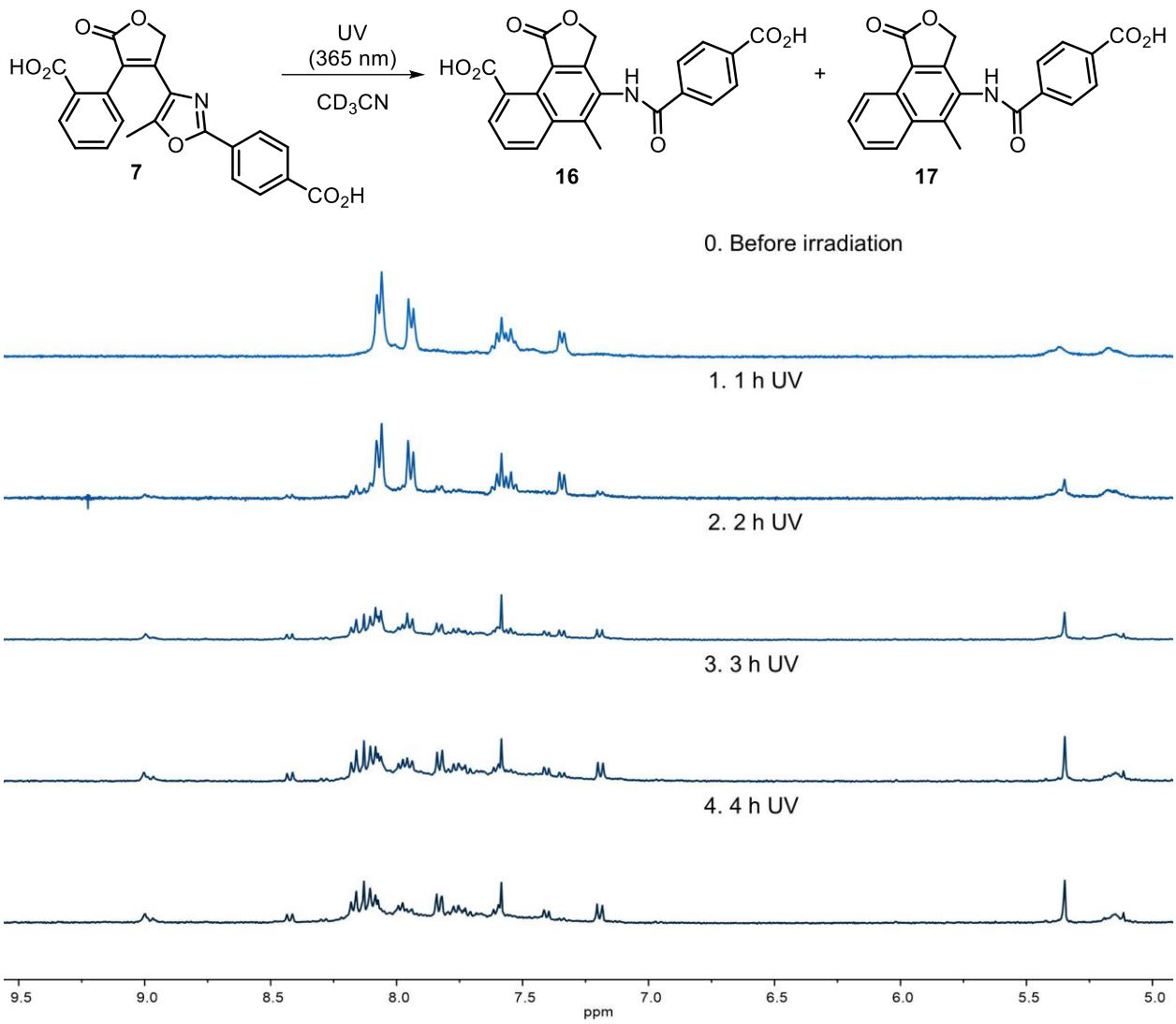


Figure S12. ^{1}H NMR monitoring of **7** irradiated by UV light (365 nm) in MeCN-d_3 over 6 h from top to bottom.

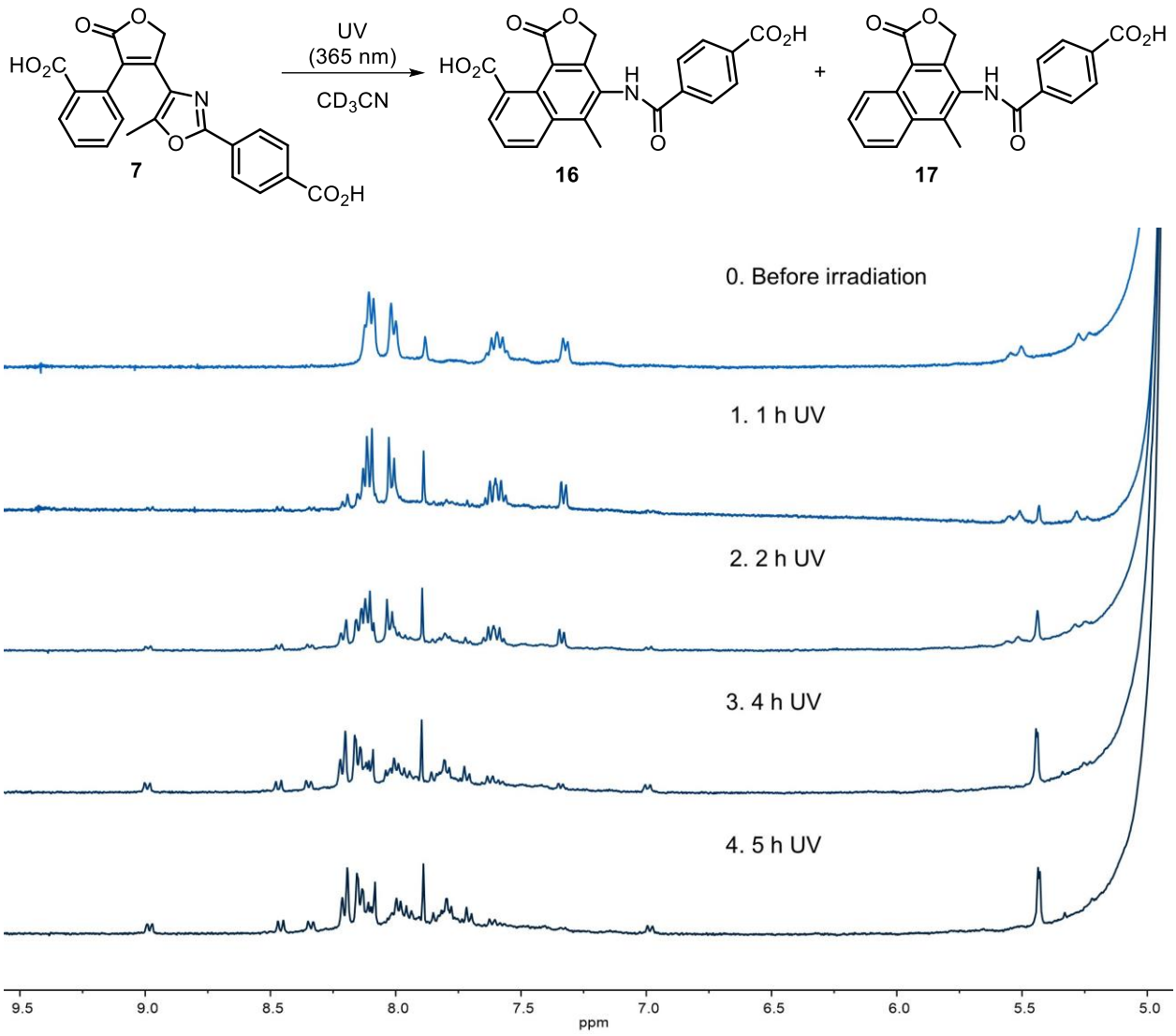


Figure S13. ^{1}H NMR monitoring of **7** irradiated by UV light (365 nm) in MeOD-d_4 over 6 h from top to bottom.

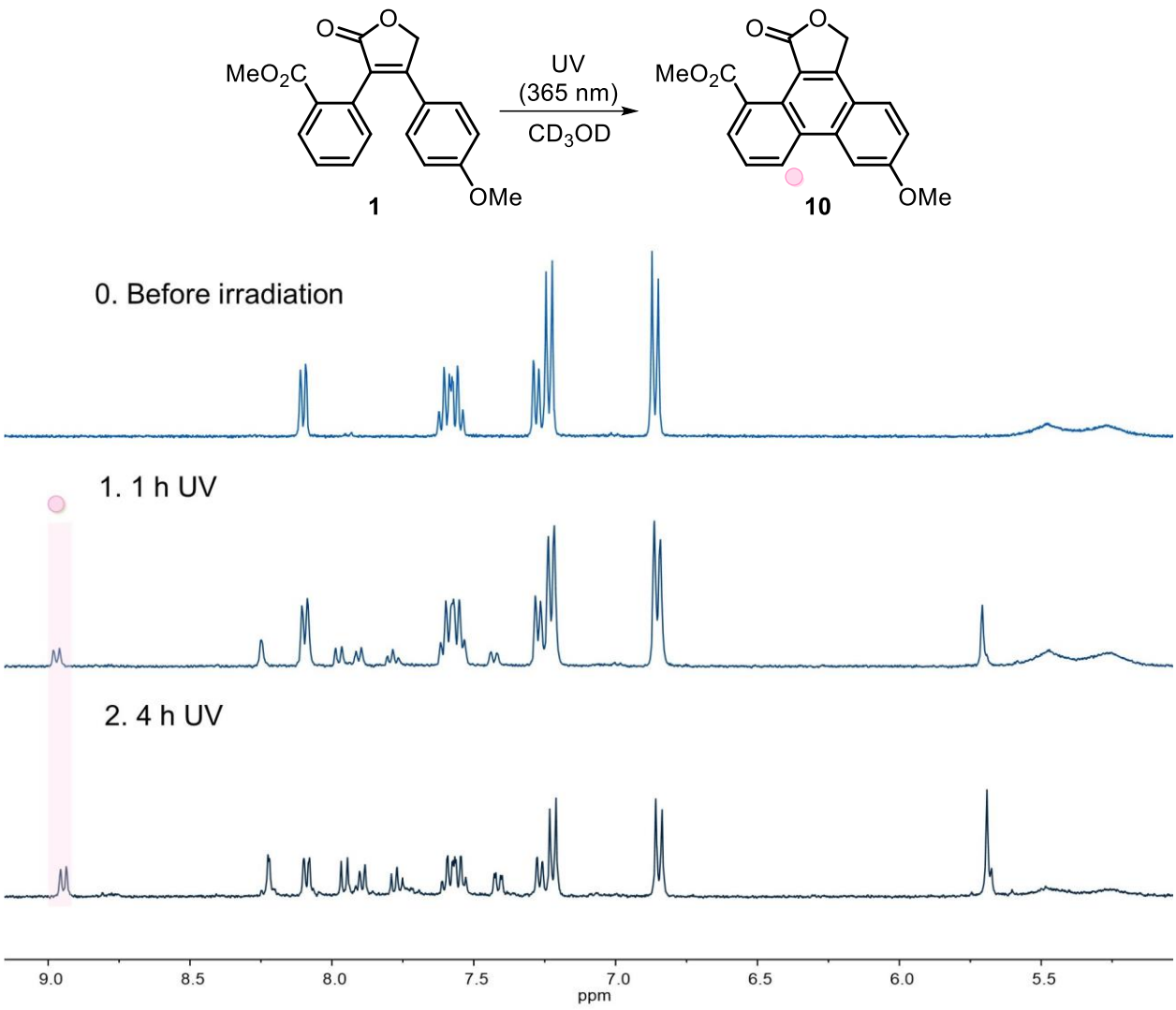


Figure S14. ^{1}H NMR monitoring of **1** irradiated by UV light (365 nm) in MeOD-d_4.

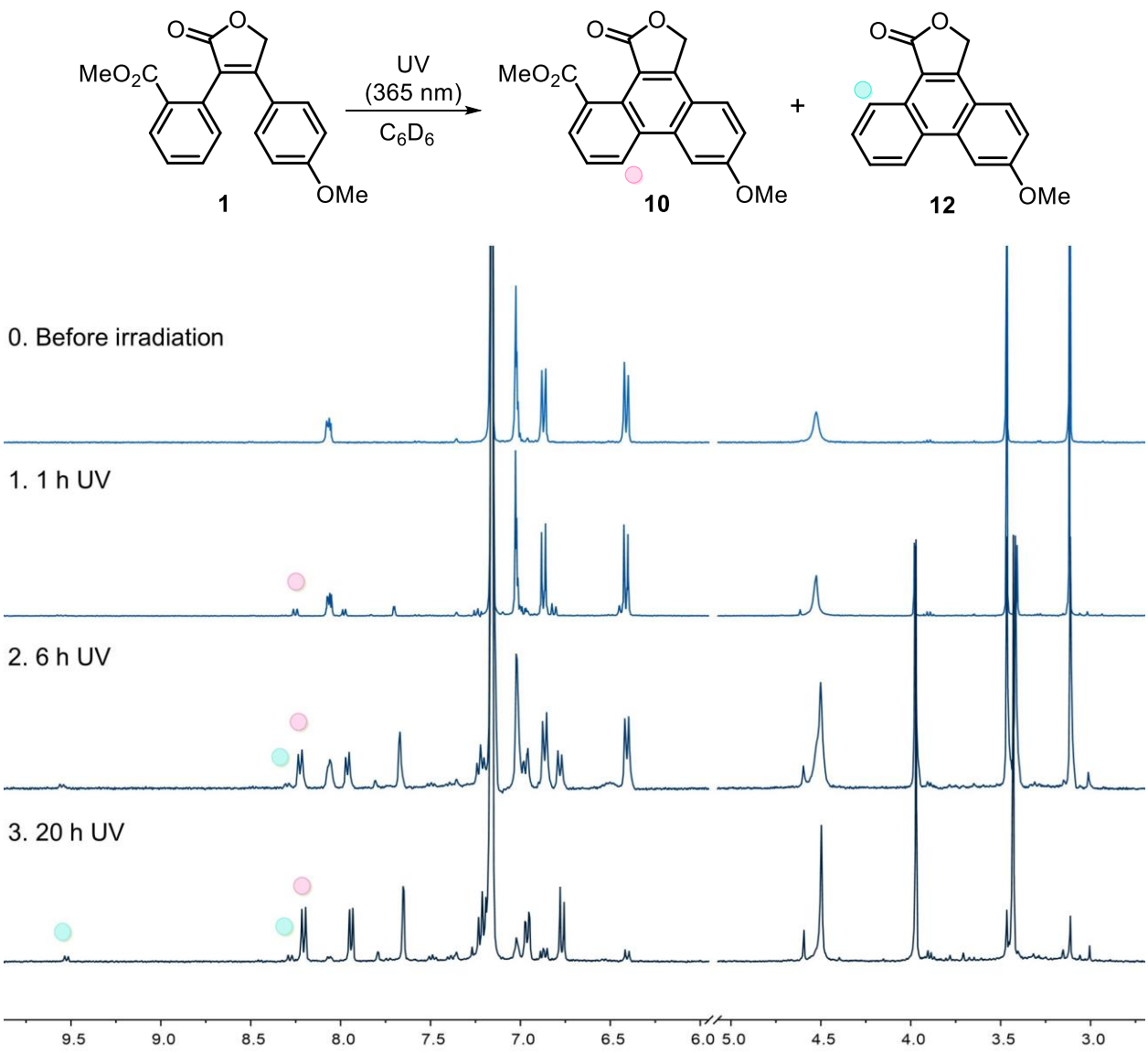


Figure S15. ^{1}H NMR monitoring of **1** irradiated by UV light (365 nm) in C_6D_6.

II.2 VT-NMR for 2

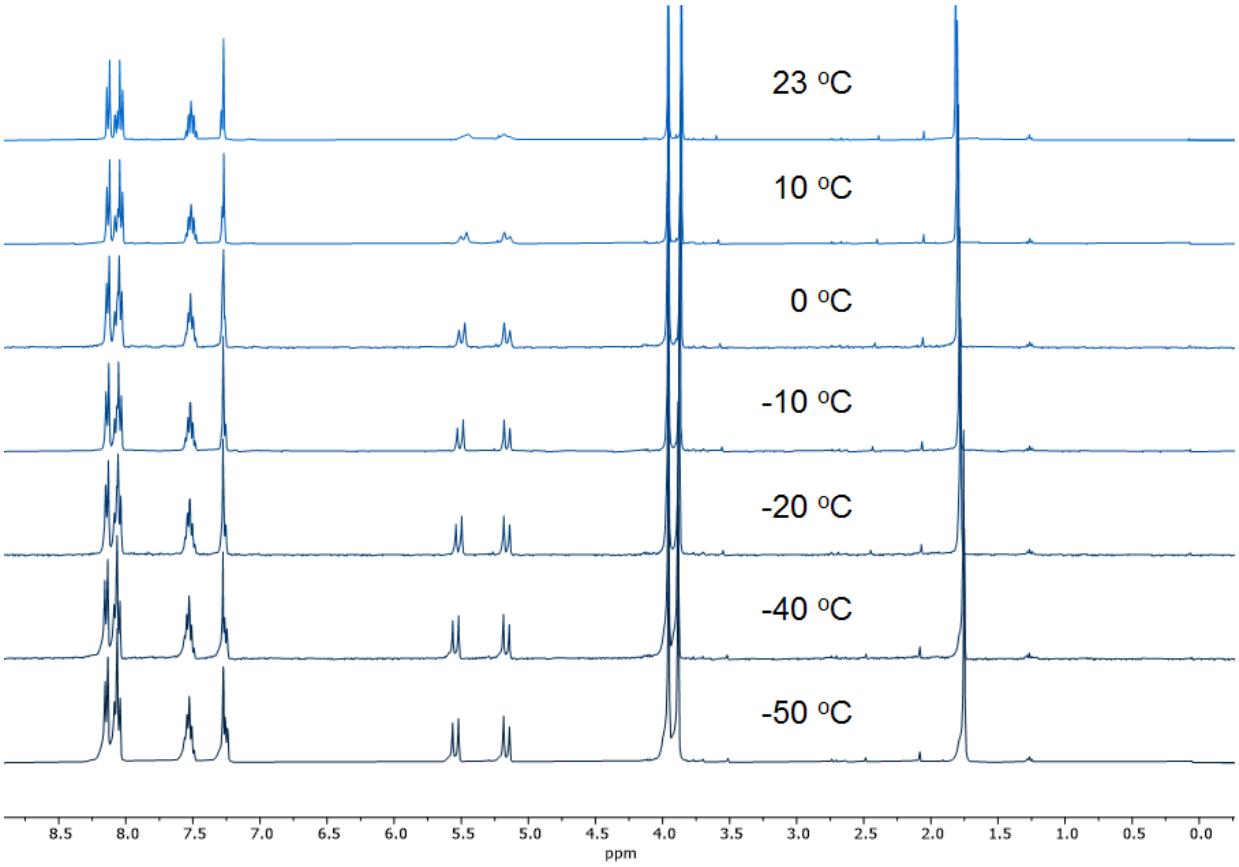
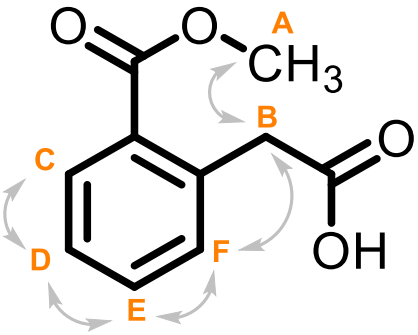


Figure S16. Changes of ^{1}H NMR spectra of **2** in $CDCl_3$ with decreasing temperature (full spectra).

II.3 2D NOESY for 4



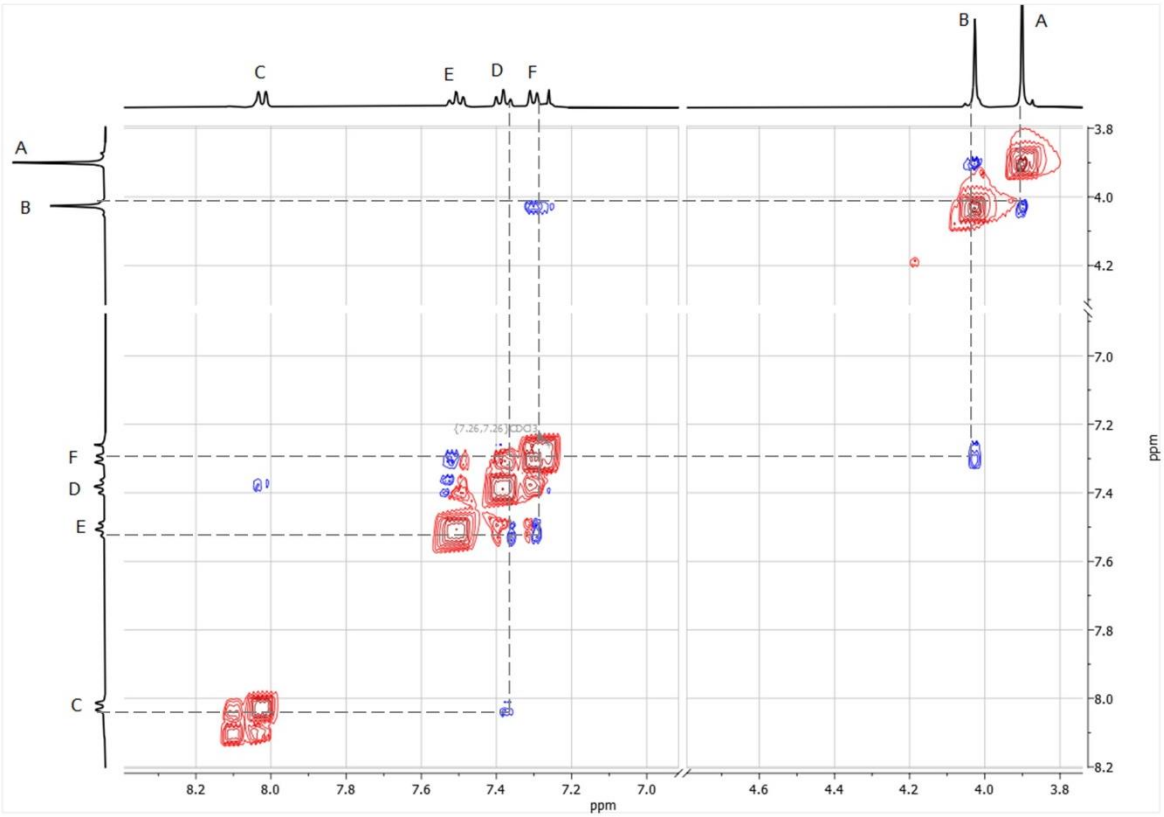


Table S1. Assignment of ^{1}H signals for **4**

	^{1}H	NOESY
A	3.90 (s, 3H)	B
B	4.03 (s, 2H)	A, F
C	8.02 (d, *J* = 6.2 Hz, 1H)	D
D	7.38 (t, *J* = 7.6 Hz, 1H)	E, C
E	7.51 (t, *J* = 7.6 Hz, 1H)	D, F
F	7.30 (d, *J* = 7.6 Hz, 1H)	B, E

III. Absorption spectroscopy

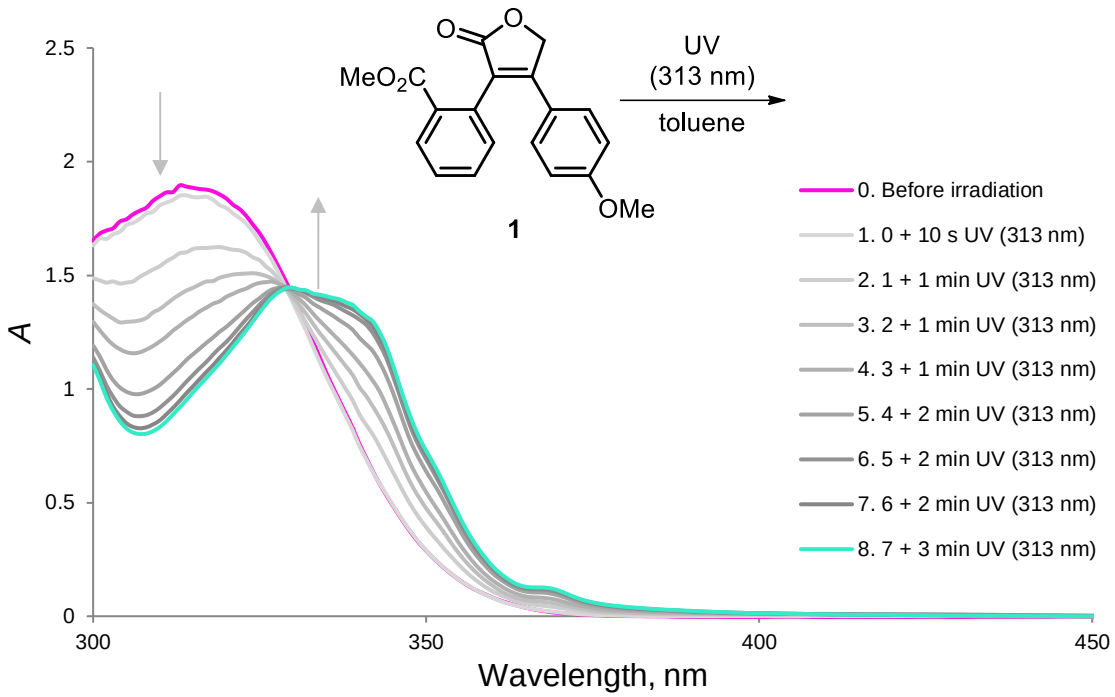


Figure S17. Spectral changes of **1** in toluene ($c \approx 10^{-4}$ M) upon irradiation with UV light (λ_{max} = 313 nm, 8 W).

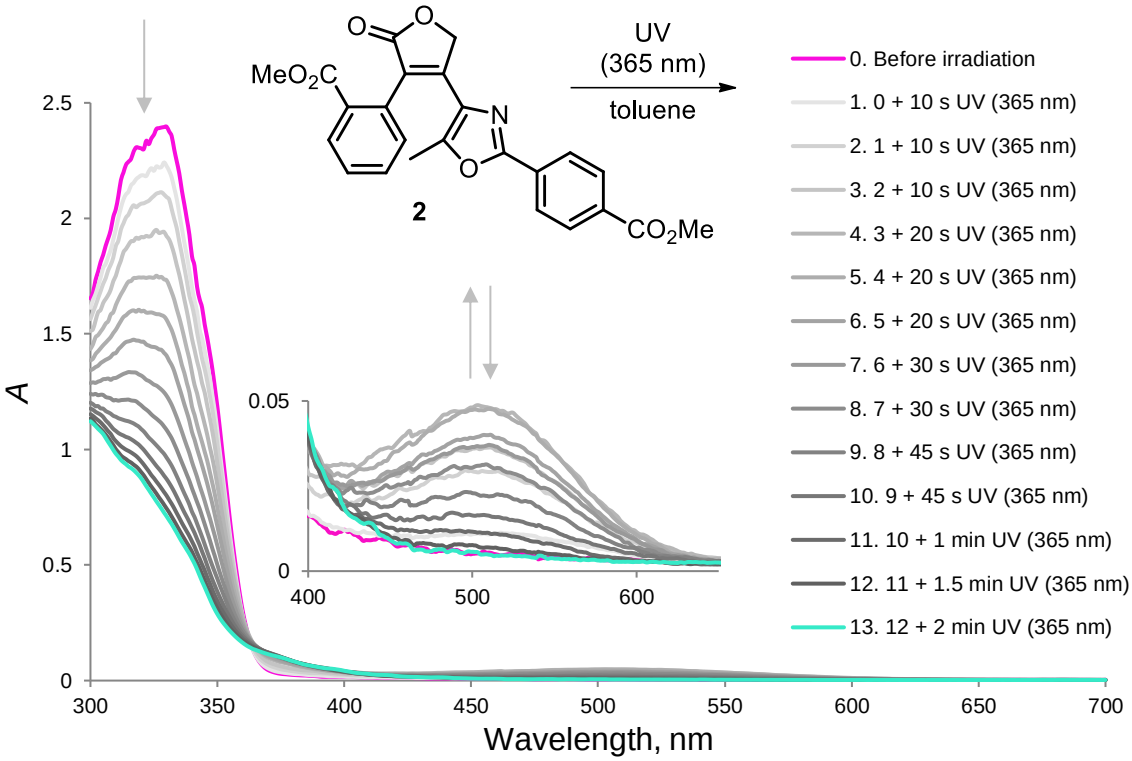


Figure S18. Spectral changes of **2** in toluene ($c \approx 10^{-4}$ M) upon irradiation with UV light (λ_{max} = 365 nm, 8 W).

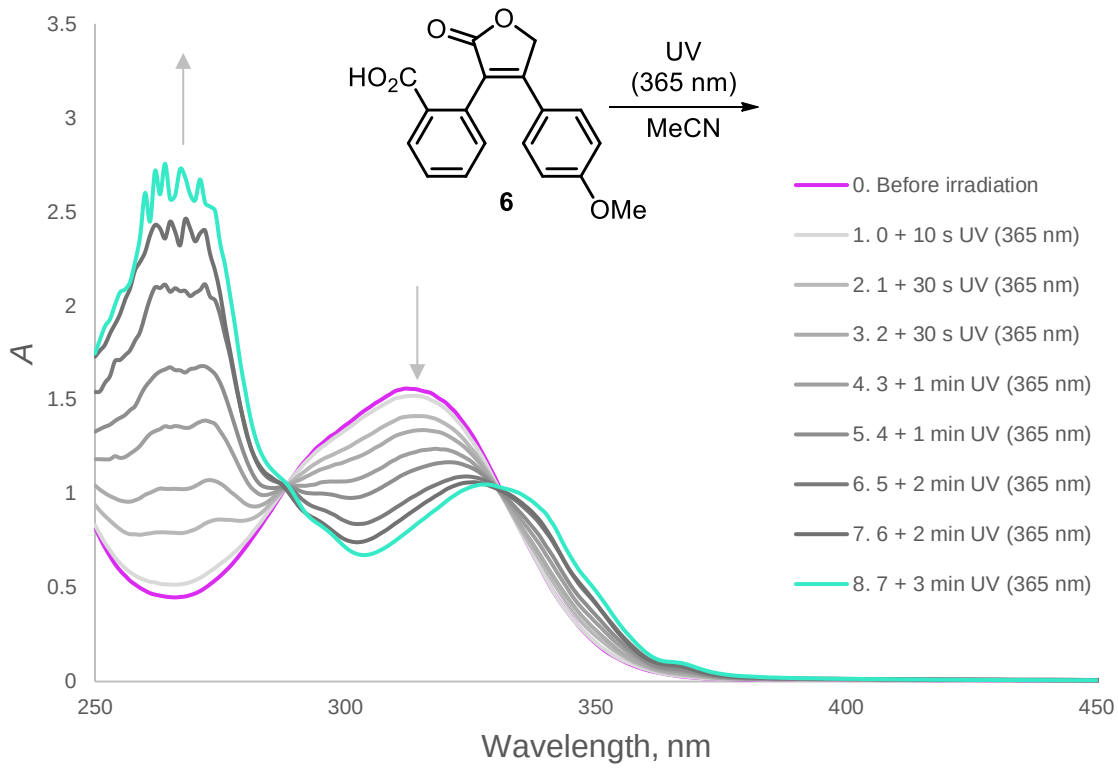


Figure S19. Spectral changes of **6** in acetonitrile ($c \approx 10^{-4}$ M) upon irradiation with UV light (λ_{max} = 365 nm, 8 W).

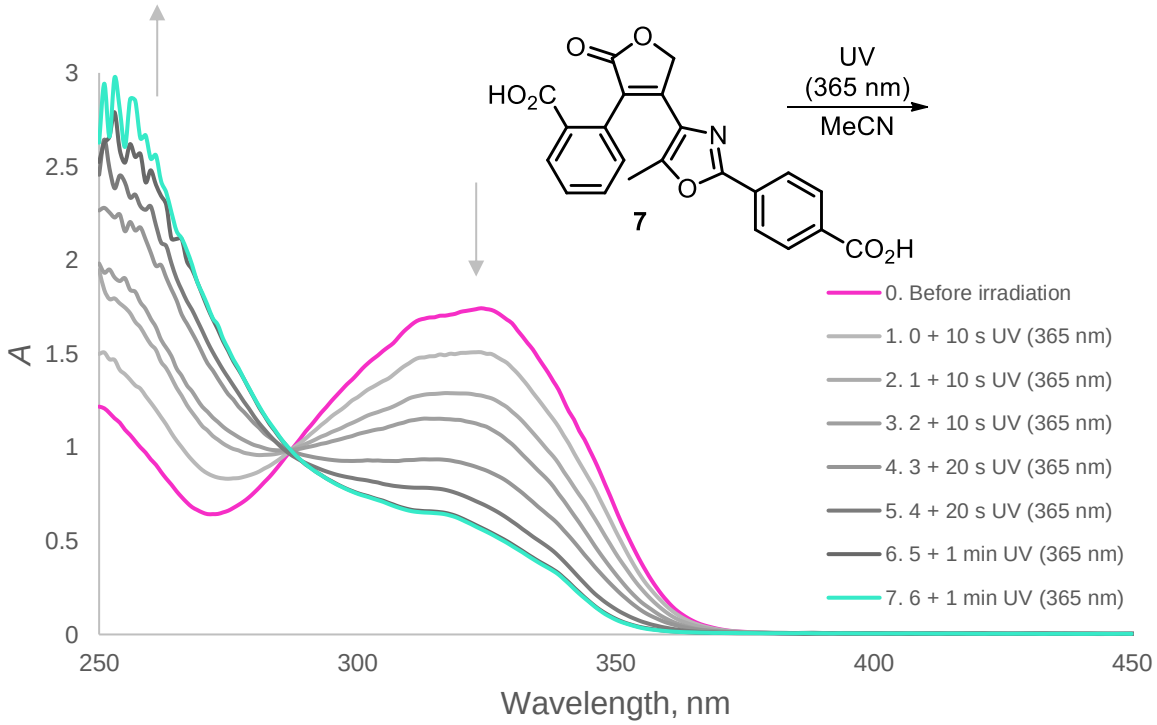


Figure S20. Spectral changes of **7** in acetonitrile ($c \approx 10^{-4}$ M) upon irradiation with UV light (λ_{max} = 365 nm, 8 W).

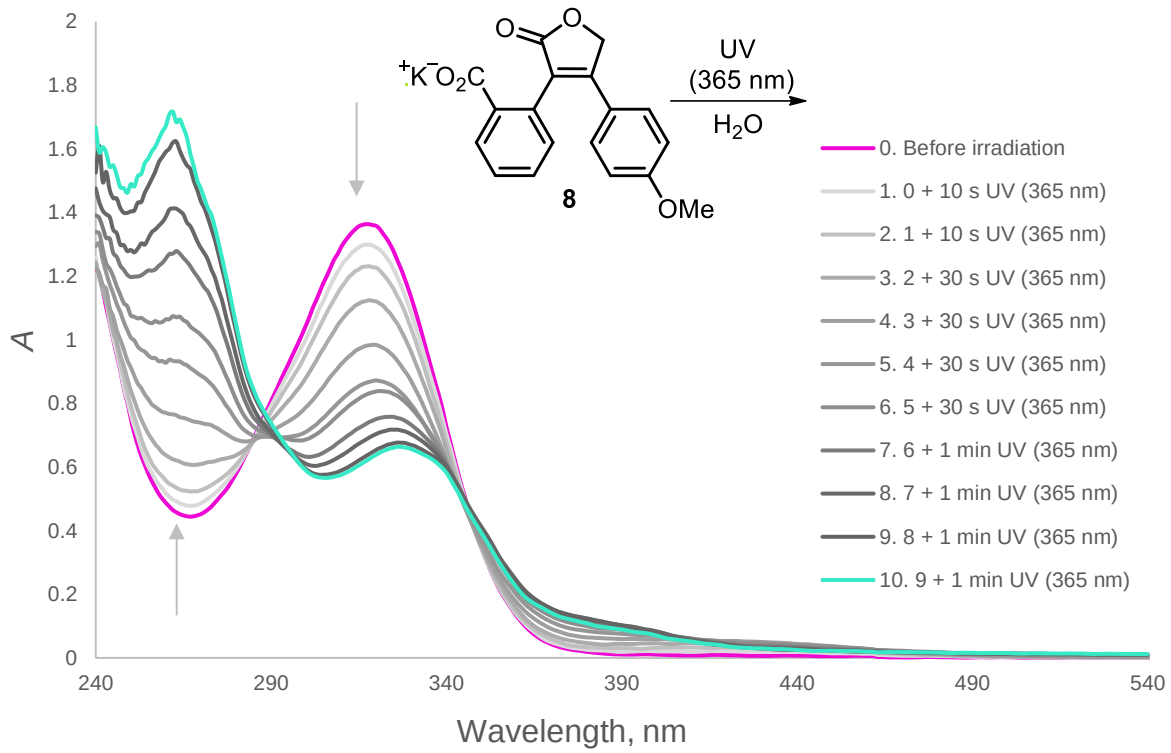


Figure S21. Spectral changes of **8** in water (buffer pH = 7, $c \approx 10^{-4}$ M) upon irradiation with UV light (λ_{max} = 365 nm, 8 W).

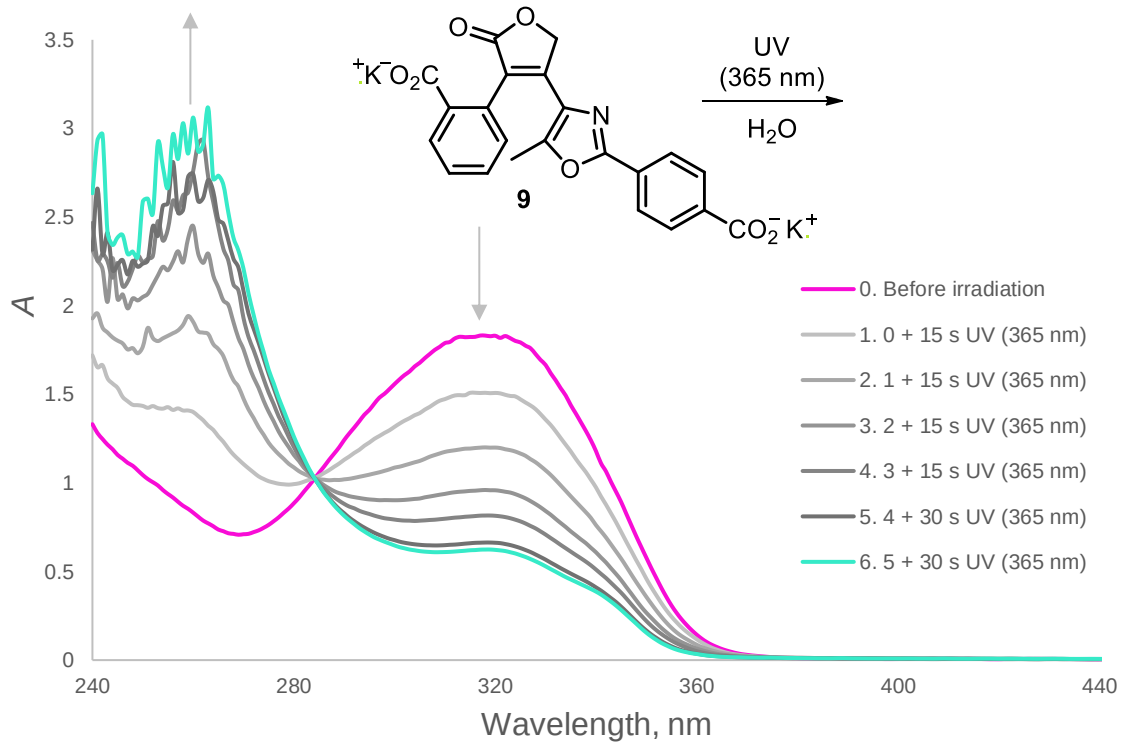


Figure S22. Spectral changes of **9** in water (buffer pH = 7, $c \approx 10^{-4}$ M) upon irradiation with UV light (λ_{max} = 365 nm, 8 W).

IV. X-ray crystallography

The X-ray diffraction experiments for compounds **1** and **2** were carried out using a SMART APEX2 CCD diffractometer (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, ω-scans) at 120 K. Collected data were processed by the SAINT and SADABS programs incorporated into the APEX2 program package. Intensities of reflections for **6** crystal were collected at 100 K at "Belok/XSA" beamline of the Kurchatov Synchrotron Radiation Source.[2,3] Diffraction pattern was collected using 1-axis MarDTB goniometer equipped with Rayonix SX165 CCD 2D positional sensitive CCD detector (λ = 0.745 Å, φ-scanning in 1.0◦ steps) in direct geometry with the detector plane perpendicular to the beam. The data were indexed and integrated using the XDS[4] software suite.

Crystal structures were solved and refined using Olex2[5] and ShelXL[6] packages. All nonhydrogen atoms were refined in anisotropic approximation against F^2(hkl). Riding hydrogens were refined in isotropic approximation.

CCDC 2467398 (**1**), 2467397 (**2**), 2467399 (**6**) contain the supplementary crystallographic data, which can be obtained free of charge at www.ccdc.cam.ac.uk/structures or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

[2] V. Lazarenko, P. Dorovatovskii, Y. Zubavichus, A. Burlov, Y. Koshchienko, V. Vlasenko and V. Khrustalev, *Crystals*, 2017, **7**, 325.

[3] R. D. Svetogorov, P. V. Dorovatovskii and V. A. Lazarenko, *Cryst. Res. Technol.*, , DOI:10.1002/crat.201900184.

[4] W. Kabsch, *Acta Crystallogr. Sect. D Biol. Crystallogr.*, 2010, **66**, 125–132.

[5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

[6] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.*, 2008, **64**, 112–122.

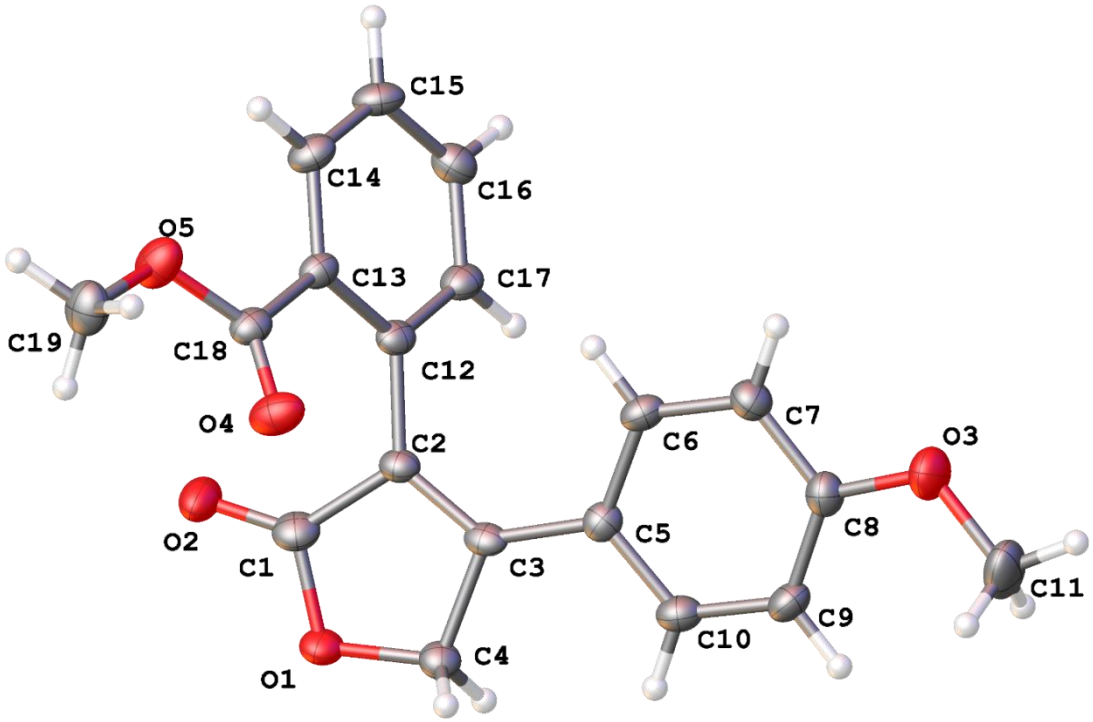


Figure S23. Molecular view and atomic numbering of **1** (ellipsoid contours of probability levels are 50%). Color code: Color code: C, gray; O, red; H white.

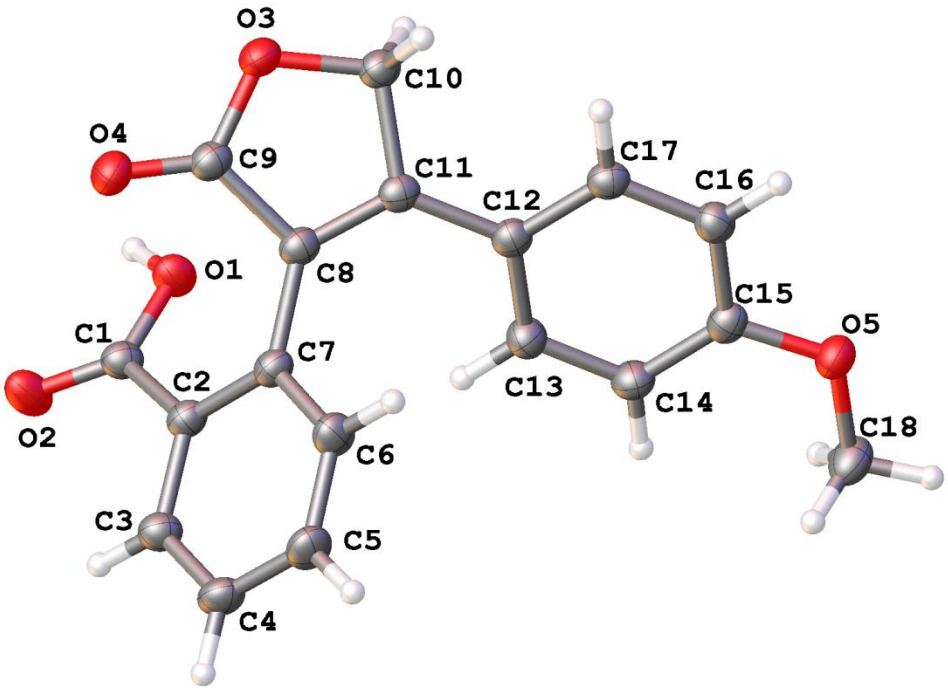


Figure S24. Molecular view and atomic numbering of **6** (ellipsoid contours of probability levels are 50%). Color code: Color code: C, gray; O, red; H white.

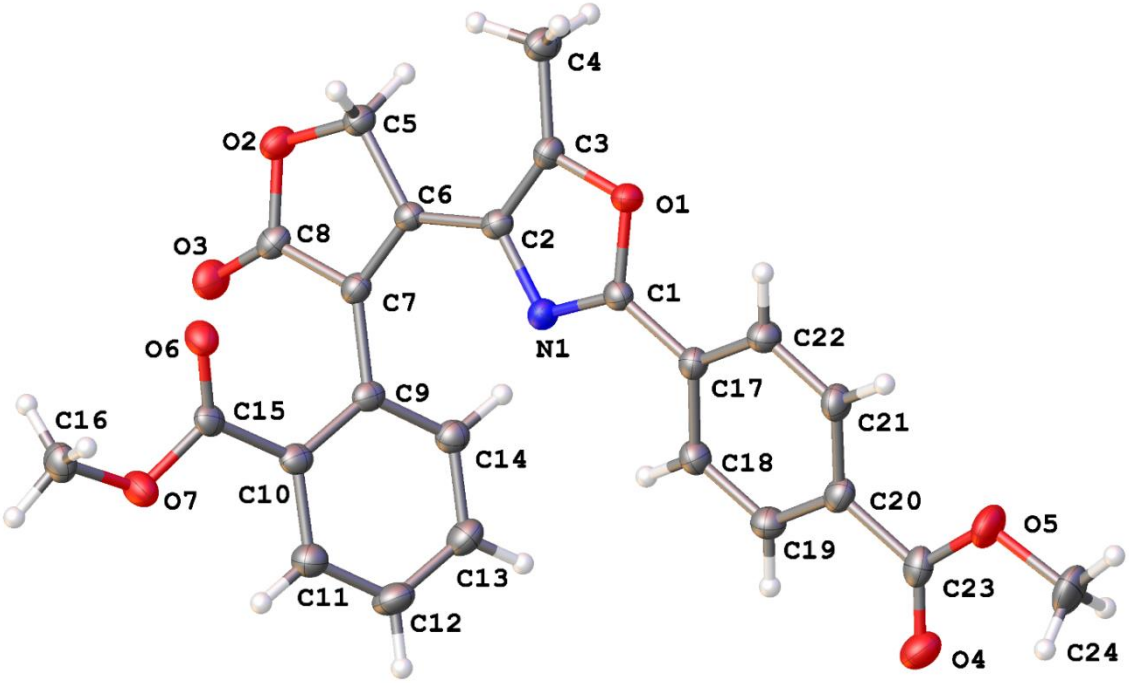


Figure S25. Molecular view and atomic numbering of **2** (ellipsoid contours of probability levels are 50%). Color code: C, gray; O, red; N, blue; H white.

Table S2. Crystal data and structure refinement for **1**, **2** and **6**.

	1	**2**	**6**
CCDC No	2467398	2467397	2467399
No	Me-148ab	Me-95	Sn-14
Formula	$C_{19}H_{16}O_5$	$C_{24}H_{19}NO_7$	$C_{18}H_{14}O_5$
F_w	324.32	433.40	310.309
T, K	120	120	100
Crystal system	monoclinic	orthorhombic	triclinic
Space group	C2/c	$Pna2_1$	P-1
a/Å	23.642(8)	7.6947(5)	7.6200(15)
b/Å	12.087(4)	17.4535(12)	7.8600(16)
c/Å	11.817(4)	14.9070(10)	13.160(3)
α/°	90	90	104.32(3)
β/°	112.960(9)	90	95.25(3)
γ/°	90	90	101.42(3)
Volume/$Å^3$	3109.2(17)	2002.0(2)	740.4(3)
Z	8	4	2
$\rho_{calc}g/cm^3$	1.386	1.438	1.392
μ/mm^{-1}	0.101	0.107	0.116
F(000)	1360.0	904.0	324.2
Crystal size/mm^3	0.24 × 0.04 × 0.03	0.22 × 0.16 × 0.11	0.15 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	synchrotron (λ = 0.75270)
2Θ range for data collection/°	3.742 to 61.18	3.594 to 61.172	3.42 to 61.78
Index ranges	$-21 \le h \le 33$, $-17 \le k \le 16$, $-16 \le l \le 16$	$-10 \le h \le 9$, $-24 \le k \le 24$, $-21 \le l \le 21$	$-10 \le h \le 10$, $-10 \le k \le 9$, $-17 \le l \le 17$
Reflections collected	13845	21640	12597
Independent reflections	4738 [R_{int} = 0.1256, R_{sigma} = 0.2150]	6045 [R_{int} = 0.0555, R_{sigma} = 0.0950]	3894 [R_{int} = 0.0402, R_{sigma} = 0.0408]
Data / restraints/ parameters	4738/0/221	6045/1/292	3894/0/210
GOF^2	1.009	0.997	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0882, wR_2 = 0.1727	R_1 = 0.0460, wR_2 = 0.0870	R_1 = 0.0420, wR_2 = 0.1098
Final R indexes [all data]	R_1 = 0.2247, wR_2 = 0.2201	R_1 = 0.0822, wR_2 = 0.0972	R_1 = 0.0500, wR_2 = 0.1168
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.51	0.23/-0.20	0.36/-0.26
Flack parameter		-0.3(6)	

Table S3. Bond Lengths for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.373(4)	C5	C6	1.419(4)
O1	C4	1.433(4)	C5	C10	1.392(4)
C1	O2	1.202(4)	C6	C7	1.370(4)
C1	C2	1.461(5)	C7	C8	1.389(4)
C2	C3	1.339(4)	C8	C9	1.392(5)
C2	C12	1.489(4)	C9	C10	1.377(5)
O3	C8	1.363(4)	C12	C13	1.419(4)
O3	C11	1.429(4)	C12	C17	1.391(4)
C3	C4	1.515(4)	C13	C14	1.382(4)
C3	C5	1.458(4)	C13	C18	1.475(4)
O4	C18	1.207(4)	C14	C15	1.378(5)
O5	C18	1.341(4)	C15	C16	1.392(5)
O5	C19	1.449(4)	C16	C17	1.382(4)

Table S4. Bond Angles for **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	O1	C4	108.4(2)	O3	C8	C7	116.0(3)
O1	C1	C2	109.1(3)	O3	C8	C9	124.0(3)
O2	C1	O1	120.3(3)	C7	C8	C9	120.0(3)
O2	C1	C2	130.6(3)	C10	C9	C8	118.9(3)
C1	C2	C12	118.9(3)	C9	C10	C5	122.9(3)
C3	C2	C1	109.1(3)	C13	C12	C2	122.5(3)
C3	C2	C12	131.9(3)	C17	C12	C2	118.9(3)
C8	O3	C11	118.0(3)	C17	C12	C13	118.3(3)
C2	C3	C4	107.5(3)	C12	C13	C18	119.8(3)
C2	C3	C5	132.3(3)	C14	C13	C12	119.3(3)
C5	C3	C4	120.0(3)	C14	C13	C18	120.9(3)
O1	C4	C3	105.7(3)	C15	C14	C13	121.8(3)
C18	O5	C19	116.3(3)	C14	C15	C16	119.3(3)
C6	C5	C3	122.3(3)	C17	C16	C15	119.8(3)
C10	C5	C3	121.0(3)	C16	C17	C12	121.6(3)
C10	C5	C6	116.6(3)	O4	C18	O5	122.7(3)
C7	C6	C5	121.2(3)	O4	C18	C13	125.4(3)
C6	C7	C8	120.4(3)	O5	C18	C13	111.7(3)

Table S5. Torsion Angles for **1**.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
O1	C1	C2	C3	-2.7(4)	C5	C6	C7	C8	0.2(5)
O1	C1	C2	C12	174.4(3)	C6	C5	C10	C9	-0.4(5)
C1	O1	C4	C3	-0.9(3)	C6	C7	C8	O3	-178.1(3)
C1	C2	C3	C4	2.1(4)	C6	C7	C8	C9	0.5(5)
C1	C2	C3	C5	-173.8(3)	C7	C8	C9	C10	-1.1(5)
C1	C2	C12	C13	60.3(4)	C8	C9	C10	C5	1.1(5)
C1	C2	C12	C17	-113.4(3)	C10	C5	C6	C7	-0.3(5)
O2	C1	C2	C3	178.1(4)	C11	O3	C8	C7	174.7(3)
O2	C1	C2	C12	-4.8(6)	C11	O3	C8	C9	-3.8(5)
C2	C3	C4	O1	-0.8(3)	C12	C2	C3	C4	-174.6(3)
C2	C3	C5	C6	7.7(6)	C12	C2	C3	C5	9.6(6)
C2	C3	C5	C10	-175.4(3)	C12	C13	C14	C15	-1.0(5)
C2	C12	C13	C14	-173.3(3)	C12	C13	C18	O4	24.7(5)
C2	C12	C13	C18	8.7(5)	C12	C13	C18	O5	-159.8(3)
C2	C12	C17	C16	174.1(3)	C13	C12	C17	C16	0.1(5)
O3	C8	C9	C10	177.3(3)	C13	C14	C15	C16	1.1(5)
C3	C2	C12	C13	-123.3(4)	C14	C13	C18	O4	-153.3(3)
C3	C2	C12	C17	63.0(5)	C14	C13	C18	O5	22.2(4)
C3	C5	C6	C7	176.8(3)	C14	C15	C16	C17	-0.6(5)
C3	C5	C10	C9	-177.5(3)	C15	C16	C17	C12	0.0(5)
C4	O1	C1	O2	-178.5(3)	C17	C12	C13	C14	0.4(5)
C4	O1	C1	C2	2.2(3)	C17	C12	C13	C18	-177.6(3)
C4	C3	C5	C6	-167.7(3)	C18	C13	C14	C15	176.9(3)
C4	C3	C5	C10	9.2(5)	C19	O5	C18	O4	-2.6(5)
C5	C3	C4	O1	175.7(3)	C19	O5	C18	C13	-178.3(3)

Table S6. Bond Lengths for **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.372(3)	O7	C16	1.447(3)
O1	C3	1.382(3)	C7	C8	1.475(3)
N1	C1	1.294(3)	C7	C9	1.481(3)
N1	C2	1.394(3)	C9	C10	1.403(3)
C1	C17	1.456(3)	C9	C14	1.391(4)
O2	C5	1.436(3)	C10	C11	1.395(4)
O2	C8	1.365(3)	C10	C15	1.489(3)
C2	C3	1.368(3)	C11	C12	1.383(4)
C2	C6	1.448(3)	C12	C13	1.378(4)
O3	C8	1.204(3)	C13	C14	1.384(3)
C3	C4	1.485(3)	C17	C18	1.398(3)
O4	C23	1.200(3)	C17	C22	1.397(4)
O5	C23	1.348(3)	C18	C19	1.387(4)
O5	C24	1.453(3)	C19	C20	1.391(3)
C5	C6	1.501(3)	C20	C21	1.387(4)
O6	C15	1.208(3)	C20	C23	1.489(4)
C6	C7	1.350(3)	C21	C22	1.381(4)
O7	C15	1.341(3)			

Table S7. Bond Angles for **2**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	O1	C3	104.99(18)	C14	C9	C7	119.5(2)
C1	N1	C2	105.41(19)	C14	C9	C10	118.9(2)
O1	C1	C17	119.0(2)	C9	C10	C15	121.3(2)
N1	C1	O1	113.5(2)	C11	C10	C9	119.4(2)
N1	C1	C17	127.5(2)	C11	C10	C15	119.0(2)
C8	O2	C5	109.07(19)	C12	C11	C10	120.7(3)
N1	C2	C6	121.3(2)	C13	C12	C11	119.8(3)
C3	C2	N1	109.0(2)	C12	C13	C14	120.2(3)
C3	C2	C6	129.6(2)	C13	C14	C9	120.9(3)
O1	C3	C4	116.5(2)	O6	C15	O7	122.5(2)
C2	C3	O1	107.1(2)	O6	C15	C10	125.4(2)
C2	C3	C4	136.4(3)	O7	C15	C10	112.0(2)
C23	O5	C24	115.6(2)	C18	C17	C1	118.4(2)
O2	C5	C6	105.29(19)	C22	C17	C1	121.8(2)
C2	C6	C5	122.4(2)	C22	C17	C18	119.7(2)
C7	C6	C2	129.0(2)	C19	C18	C17	120.0(2)
C7	C6	C5	108.5(2)	C18	C19	C20	120.0(2)
C15	O7	C16	115.9(2)	C19	C20	C23	118.1(2)
C6	C7	C8	107.9(2)	C21	C20	C19	119.8(2)
C6	C7	C9	131.6(2)	C21	C20	C23	122.1(2)
C8	C7	C9	120.5(2)	C22	C21	C20	120.8(3)
O2	C8	C7	109.0(2)	C21	C22	C17	119.7(2)
O3	C8	O2	121.6(2)	O4	C23	O5	123.3(2)
O3	C8	C7	129.3(2)	O4	C23	C20	125.0(3)
C10	C9	C7	121.5(2)	O5	C23	C20	111.7(2)

Table S8. Torsion Angles for **2**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C1	C17	C18	-166.9(2)	C7	C9	C10	C15	-8.0(4)
O1	C1	C17	C22	11.4(4)	C7	C9	C14	C13	-178.0(2)
N1	C1	C17	C18	10.1(4)	C8	O2	C5	C6	4.0(3)
N1	C1	C17	C22	-171.6(3)	C8	C7	C9	C10	-59.9(3)
N1	C2	C3	O1	0.0(3)	C8	C7	C9	C14	117.8(3)
N1	C2	C3	C4	176.7(3)	C9	C7	C8	O2	179.4(2)
N1	C2	C6	C5	-179.5(2)	C9	C7	C8	O3	-2.6(4)
N1	C2	C6	C7	4.3(4)	C9	C10	C11	C12	-0.2(4)
C1	O1	C3	C2	0.3(3)	C9	C10	C15	O6	-14.8(4)
C1	O1	C3	C4	-177.2(2)	C9	C10	C15	O7	168.0(2)
C1	N1	C2	C3	-0.3(3)	C10	C9	C14	C13	-0.3(4)
C1	N1	C2	C6	179.5(2)	C10	C11	C12	C13	0.7(4)
C1	C17	C18	C19	177.1(2)	C11	C10	C15	O6	159.5(3)
C1	C17	C22	C21	-177.4(3)	C11	C10	C15	O7	-17.7(3)
O2	C5	C6	C2	178.5(2)	C11	C12	C13	C14	-1.0(4)
O2	C5	C6	C7	-4.6(3)	C12	C13	C14	C9	0.8(4)
C2	N1	C1	O1	0.5(3)	C14	C9	C10	C11	0.0(4)
C2	N1	C1	C17	-176.6(2)	C14	C9	C10	C15	174.3(2)
C2	C6	C7	C8	-180.0(2)	C15	C10	C11	C12	-174.7(2)
C2	C6	C7	C9	-0.3(5)	C16	O7	C15	O6	-6.7(3)
C3	O1	C1	N1	-0.5(3)	C16	O7	C15	C10	170.6(2)
C3	O1	C1	C17	176.9(2)	C17	C18	C19	C20	0.5(4)
C3	C2	C6	C5	0.4(4)	C18	C17	C22	C21	0.9(4)
C3	C2	C6	C7	-175.8(3)	C18	C19	C20	C21	0.6(4)
C5	O2	C8	O3	179.7(2)	C18	C19	C20	C23	-177.9(2)
C5	O2	C8	C7	-2.1(3)	C19	C20	C21	C22	-1.0(4)
C5	C6	C7	C8	3.4(3)	C19	C20	C23	O4	-8.2(4)
C5	C6	C7	C9	-176.9(3)	C19	C20	C23	O5	172.6(2)
C6	C2	C3	O1	-179.8(2)	C20	C21	C22	C17	0.3(4)
C6	C2	C3	C4	-3.1(5)	C21	C20	C23	O4	173.4(3)
C6	C7	C8	O2	-0.9(3)	C21	C20	C23	O5	-5.9(4)
C6	C7	C8	O3	177.1(3)	C22	C17	C18	C19	-1.3(4)
C6	C7	C9	C10	120.4(3)	C23	C20	C21	C22	177.4(3)
C6	C7	C9	C14	-61.9(4)	C24	O5	C23	O4	2.1(4)
C7	C9	C10	C11	177.7(2)	C24	O5	C23	C20	-178.6(2)

Table S9. Bond Lengths for **6**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	O1	1.3125(15)	C6	C7	1.3996(16)
C1	C2	1.4897(16)	C7	C8	1.4774(17)
C1	O2	1.2277(15)	C8	C9	1.4786(16)
C2	C3	1.3955(17)	C8	C11	1.3450(17)
C2	C7	1.4040(16)	C10	C11	1.5005(16)
C3	C4	1.3852(16)	C11	C12	1.4622(16)
O3	C9	1.3610(15)	C12	C13	1.3972(17)
O3	C10	1.4382(15)	C12	C17	1.4017(16)
C4	C5	1.3833(19)	C13	C14	1.3847(17)
O4	C9	1.2036(15)	C14	C15	1.3891(17)
C5	C6	1.3869(18)	C15	C16	1.3981(17)
O5	C15	1.3603(14)	C16	C17	1.3804(16)
O5	C18	1.4347(16)			

Table S10. Bond Angles for **6**.

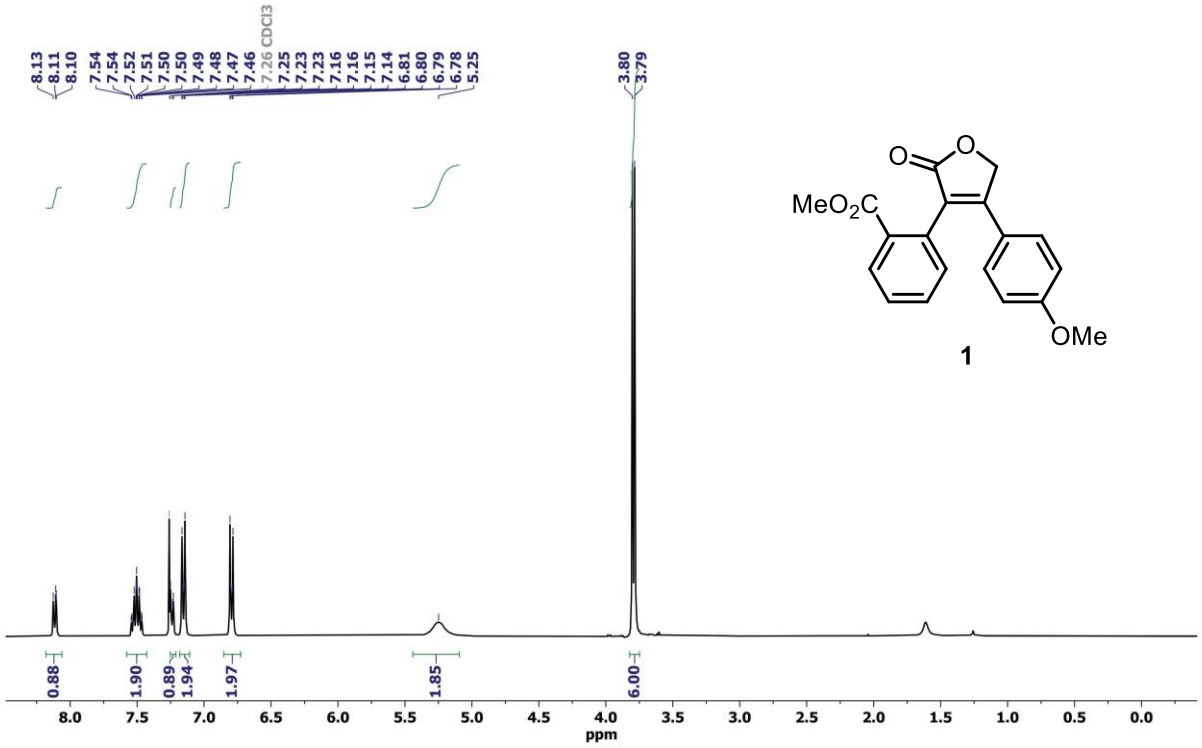
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	O1	115.42(10)	O4	C9	O3	121.85(11)
O2	C1	O1	123.25(10)	C8	C9	O3	108.73(10)
O2	C1	C2	121.25(10)	C8	C9	O4	129.41(11)
C3	C2	C1	116.43(10)	C11	C10	O3	105.13(9)
C7	C2	C1	123.67(10)	C10	C11	C8	108.65(10)
C7	C2	C3	119.87(10)	C12	C11	C8	130.25(10)
C4	C3	C2	121.06(11)	C12	C11	C10	121.07(10)
C10	O3	C9	109.38(9)	C13	C12	C11	120.95(10)
C5	C4	C3	119.29(11)	C17	C12	C11	121.05(10)
C6	C5	C4	120.31(11)	C17	C12	C13	117.98(10)
C18	O5	C15	117.11(9)	C14	C13	C12	121.70(11)
C7	C6	C5	121.19(11)	C15	C14	C13	119.34(11)
C6	C7	C2	118.21(11)	C14	C15	O5	124.19(11)
C8	C7	C2	123.68(10)	C16	C15	O5	115.77(10)
C8	C7	C6	117.98(10)	C16	C15	C14	120.03(11)
C9	C8	C7	121.13(10)	C17	C16	C15	119.99(11)
C11	C8	C7	130.48(10)	C16	C17	C12	120.93(11)
C11	C8	C9	108.11(10)				

Table S11. Torsion Angles for **6**.

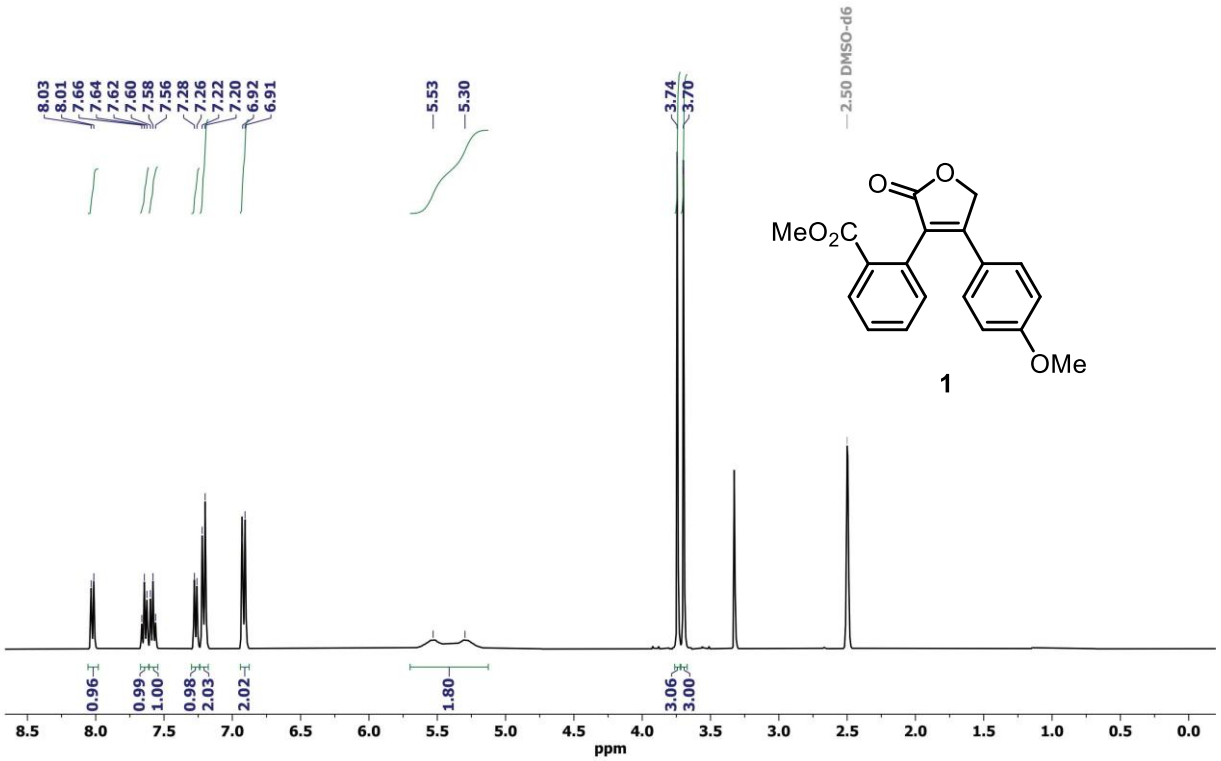
A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
C1	C2	C3	C4	174.93(11)	O5	C15	C14	C13	179.77(11)
C1	C2	C7	C6	-175.23(12)	O5	C15	C16	C17	179.10(10)
C1	C2	C7	C8	8.95(14)	C6	C7	C8	C9	-123.46(11)
C2	C3	C4	C5	0.91(15)	C6	C7	C8	C11	49.81(14)
C2	C7	C6	C5	-0.06(13)	C7	C8	C11	C10	-173.94(13)
C2	C7	C8	C9	52.37(13)	C7	C8	C11	C12	8.33(16)
C2	C7	C8	C11	-134.36(12)	C8	C11	C12	C13	27.39(15)
C3	C4	C5	C6	1.50(15)	C8	C11	C12	C17	-154.45(12)
O3	C9	C8	C7	174.60(8)	C10	C11	C12	C13	-150.10(11)
O3	C9	C8	C11	-0.02(10)	C10	C11	C12	C17	28.06(12)
O3	C10	C11	C8	0.02(10)	C11	C12	C13	C14	178.63(11)
O3	C10	C11	C12	177.99(8)	C11	C12	C17	C16	-179.85(10)
C4	C5	C6	C7	-1.93(16)	C12	C13	C14	C15	0.94(14)
O4	C9	C8	C7	-3.86(16)	C12	C17	C16	C15	1.50(13)
O4	C9	C8	C11	-178.48(14)	C13	C14	C15	C16	-1.09(14)
C5	C6	C7	C8	176.00(12)	C14	C15	C16	C17	-0.12(13)

V. Copies of NMR spectra

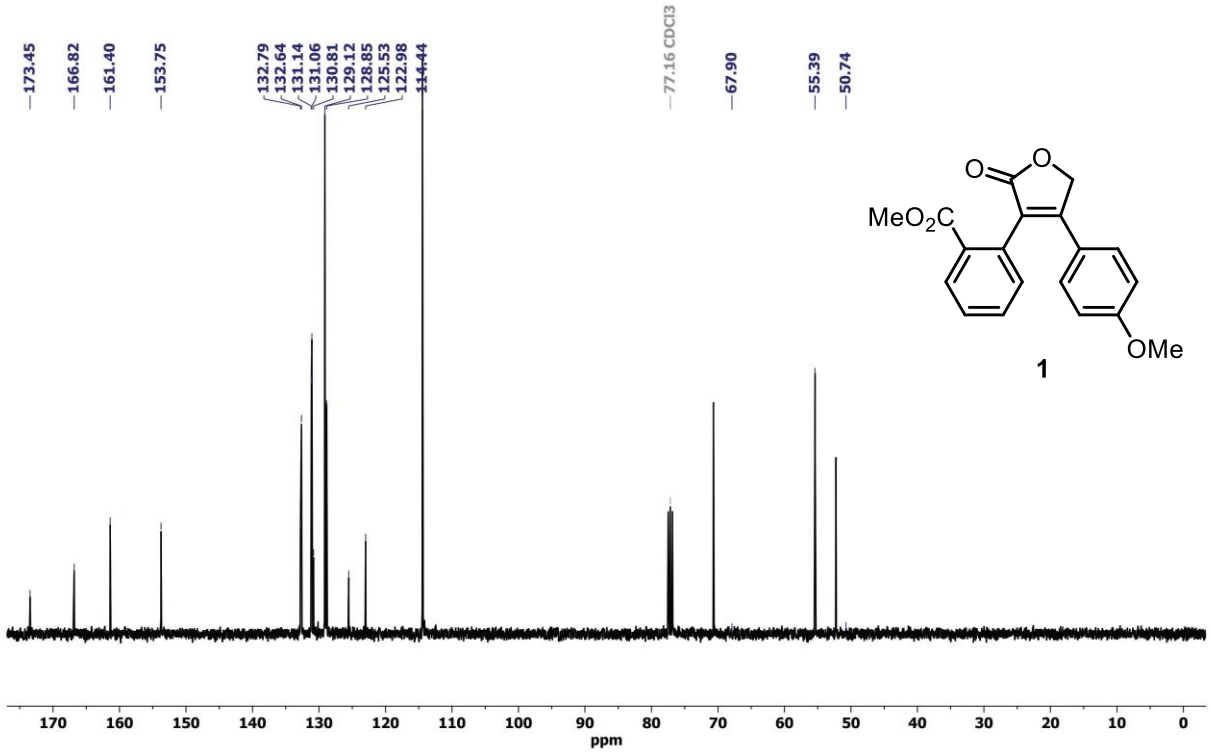
^{1}H NMR spectrum of **1** in $CDCl_3$



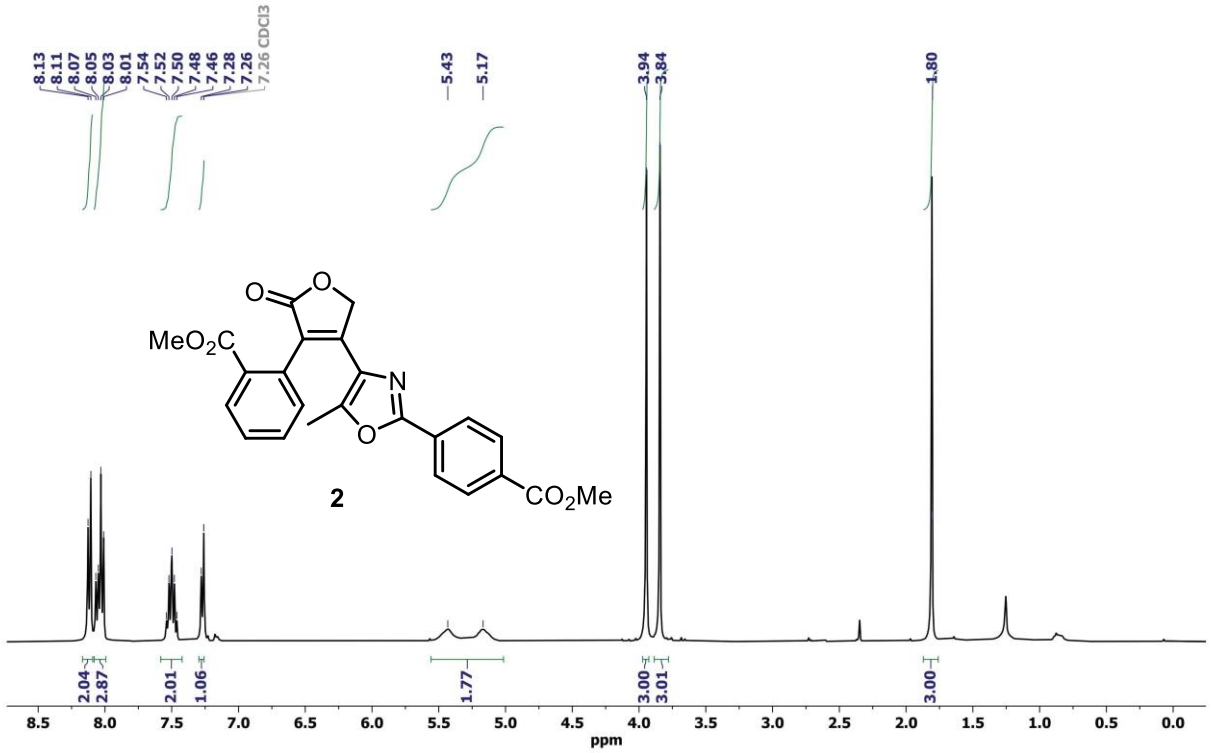
^{1}H NMR spectrum of **1** in DMSO-d_6



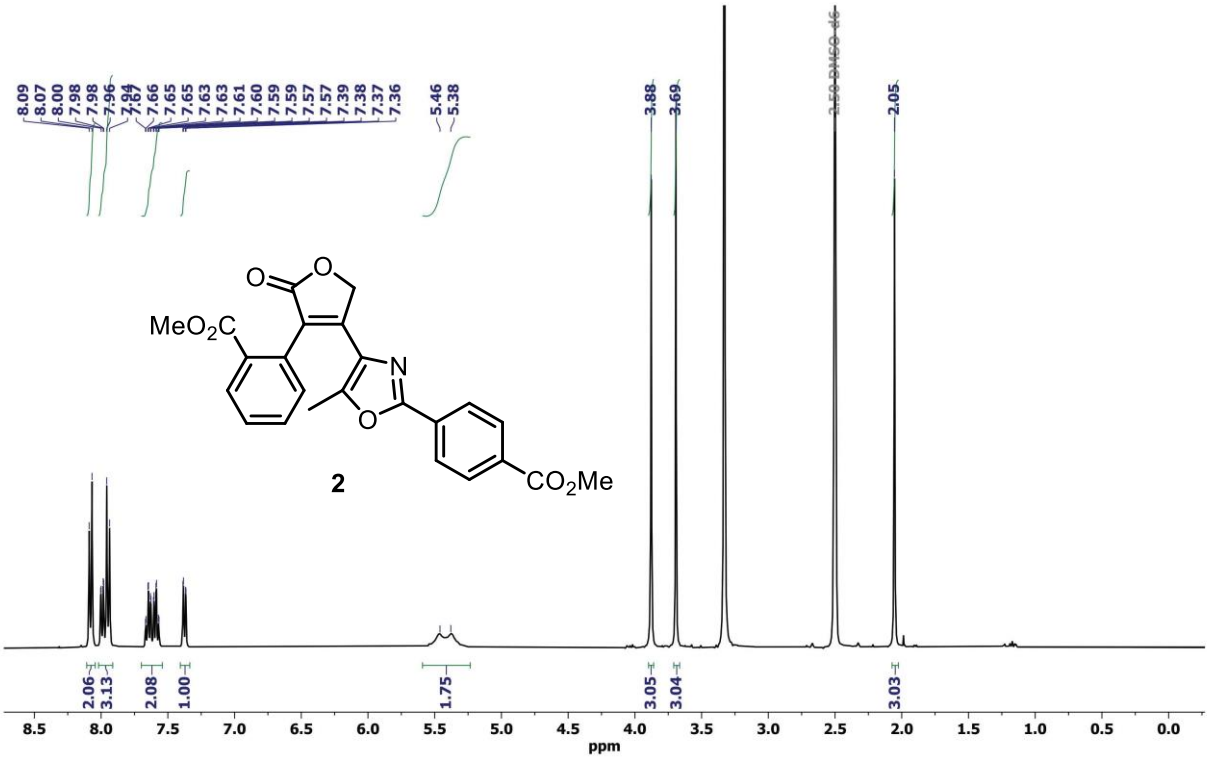
$^{13}C\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$



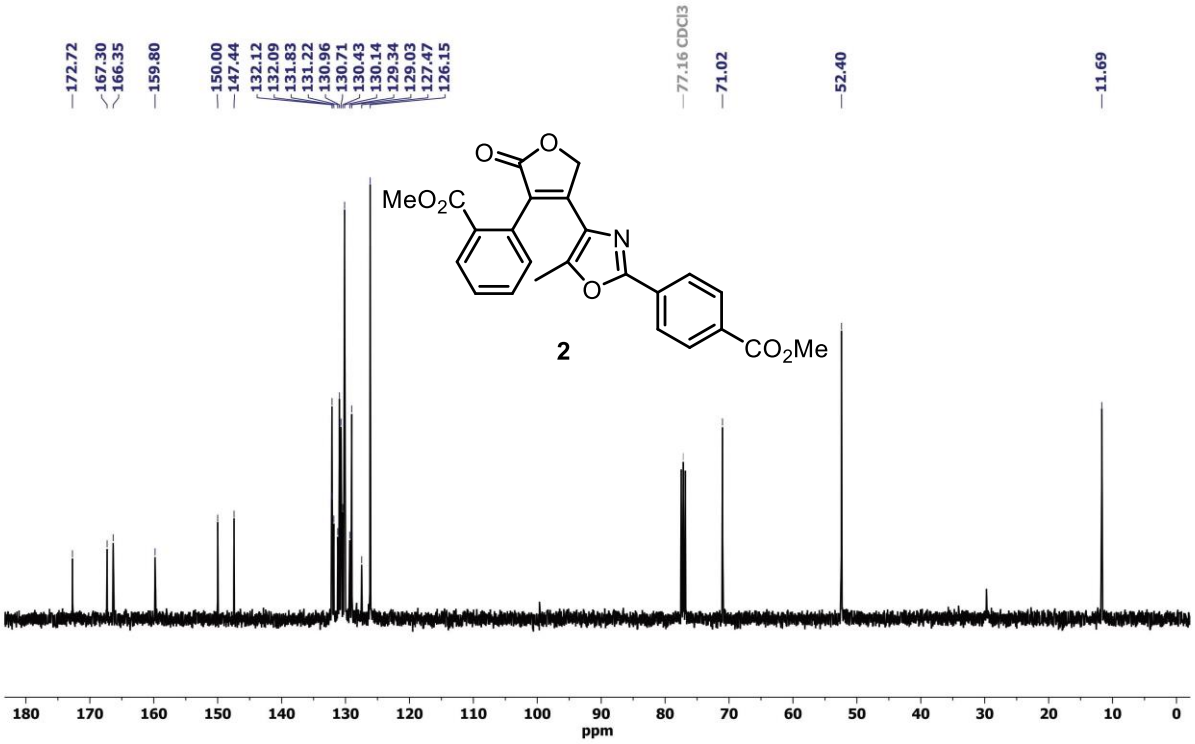
^{1}H NMR spectrum of **2** in $CDCl_3$



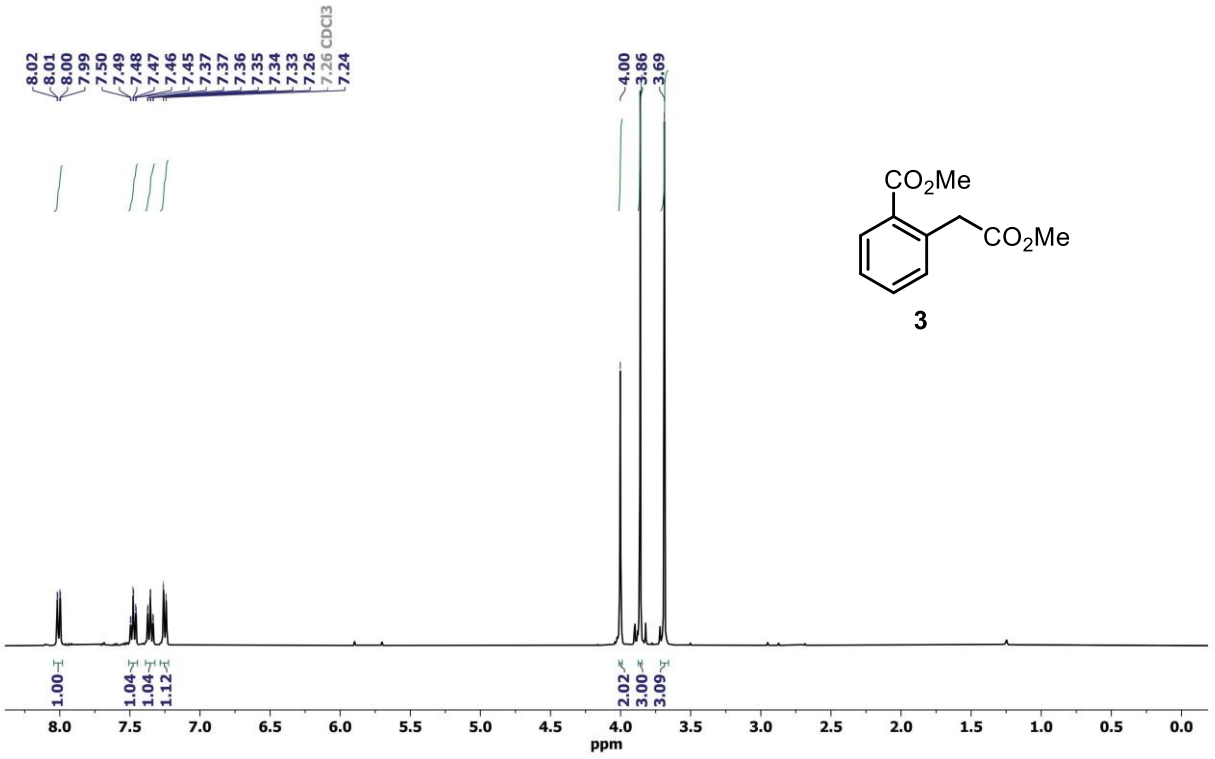
^{1}H NMR spectrum of **2** in DMSO-d_6



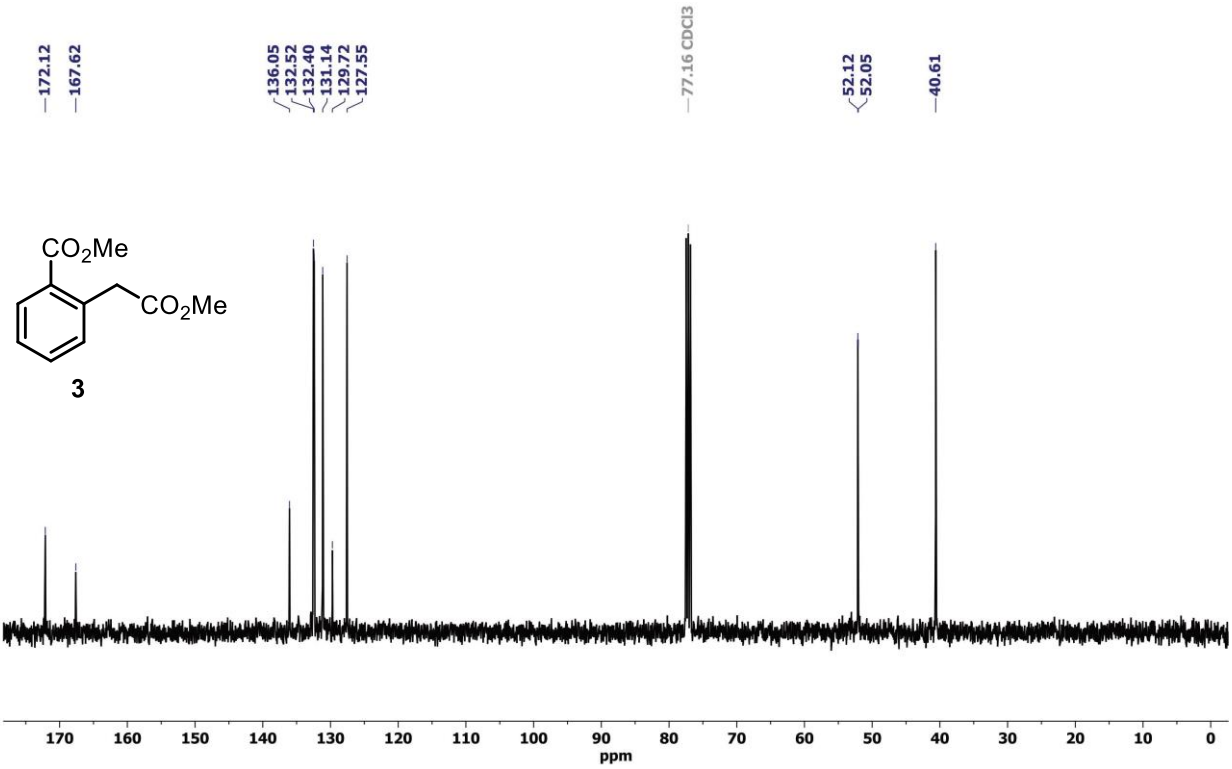
$^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$



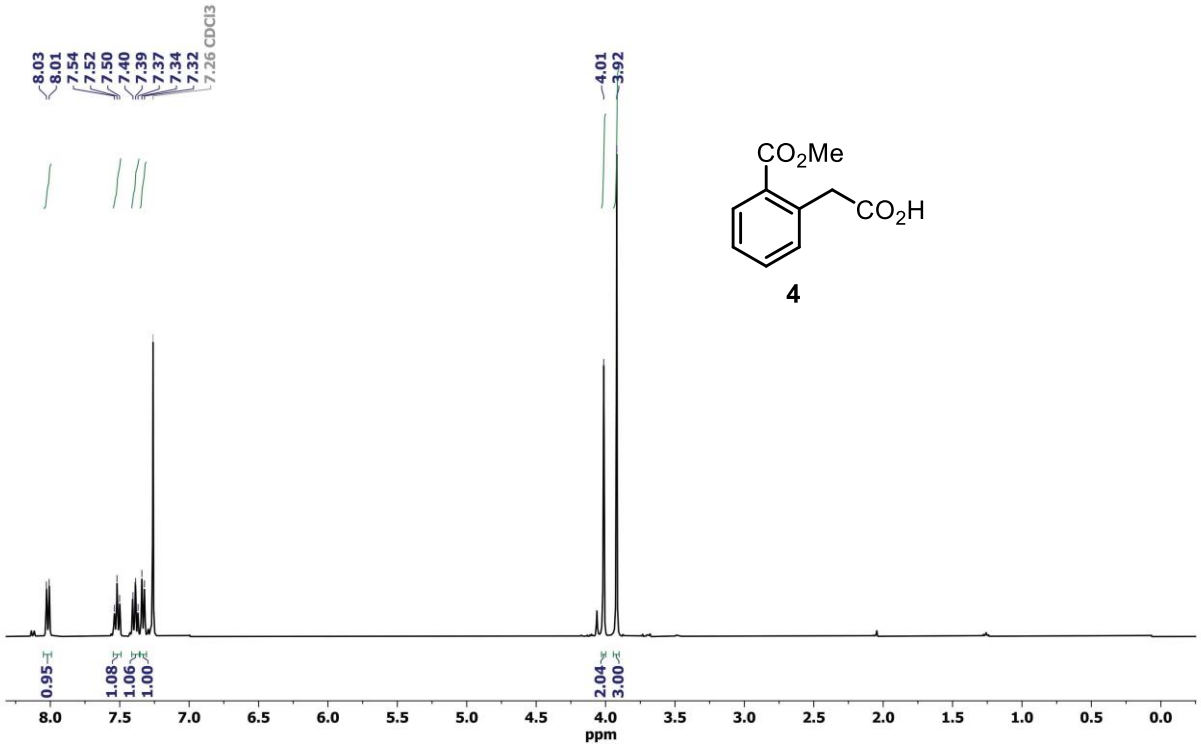
^{1}H NMR spectrum of **3** in $CDCl_3$



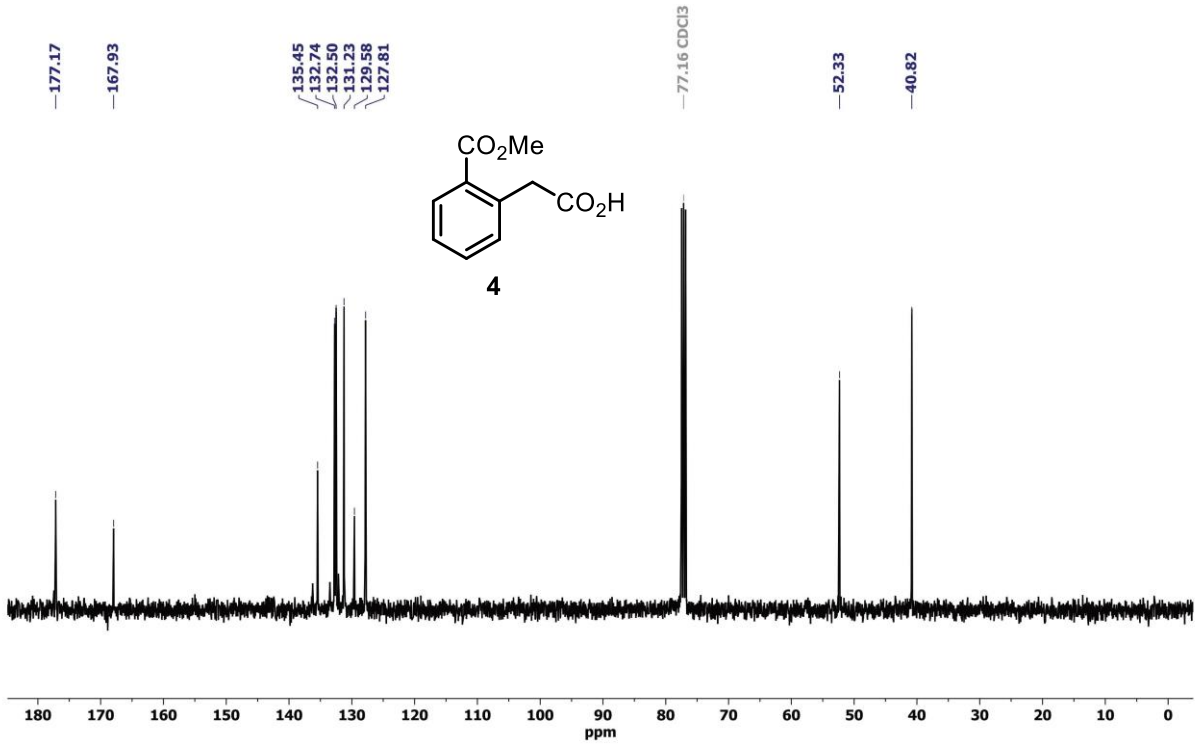
^{13}C{^{1}H} NMR spectrum of **3** in $CDCl_3$



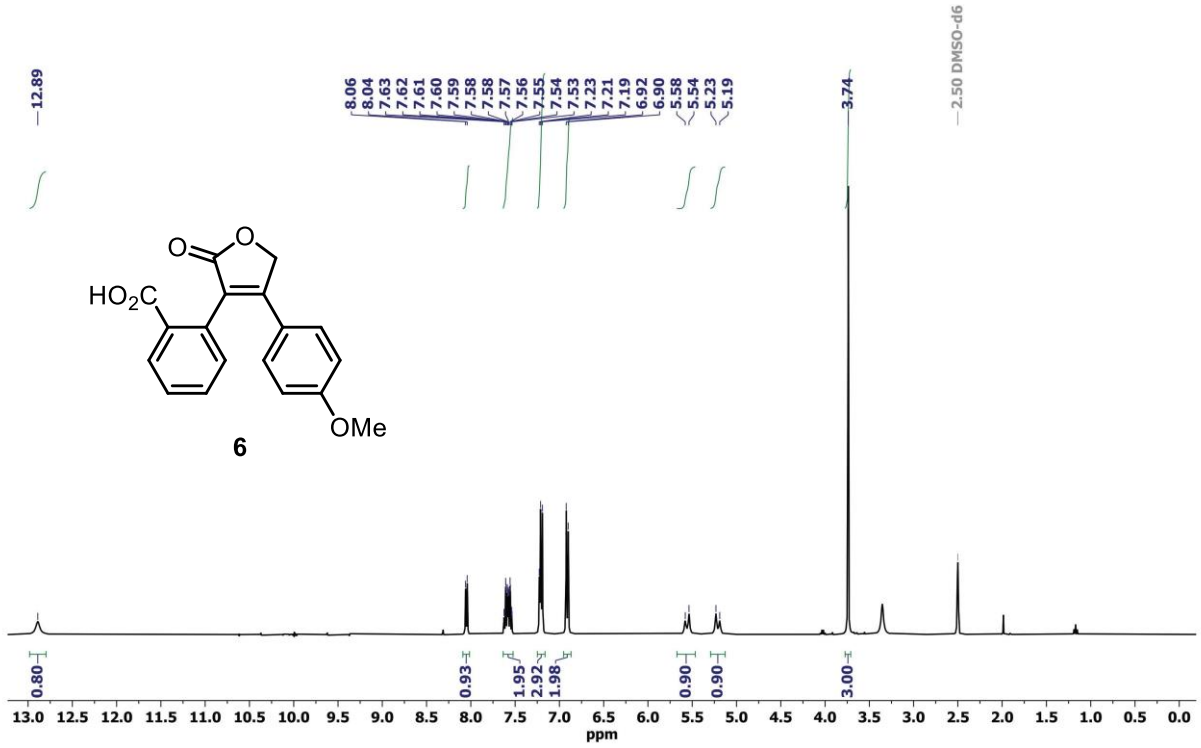
^{1}H NMR spectrum of **4** in $CDCl_3$



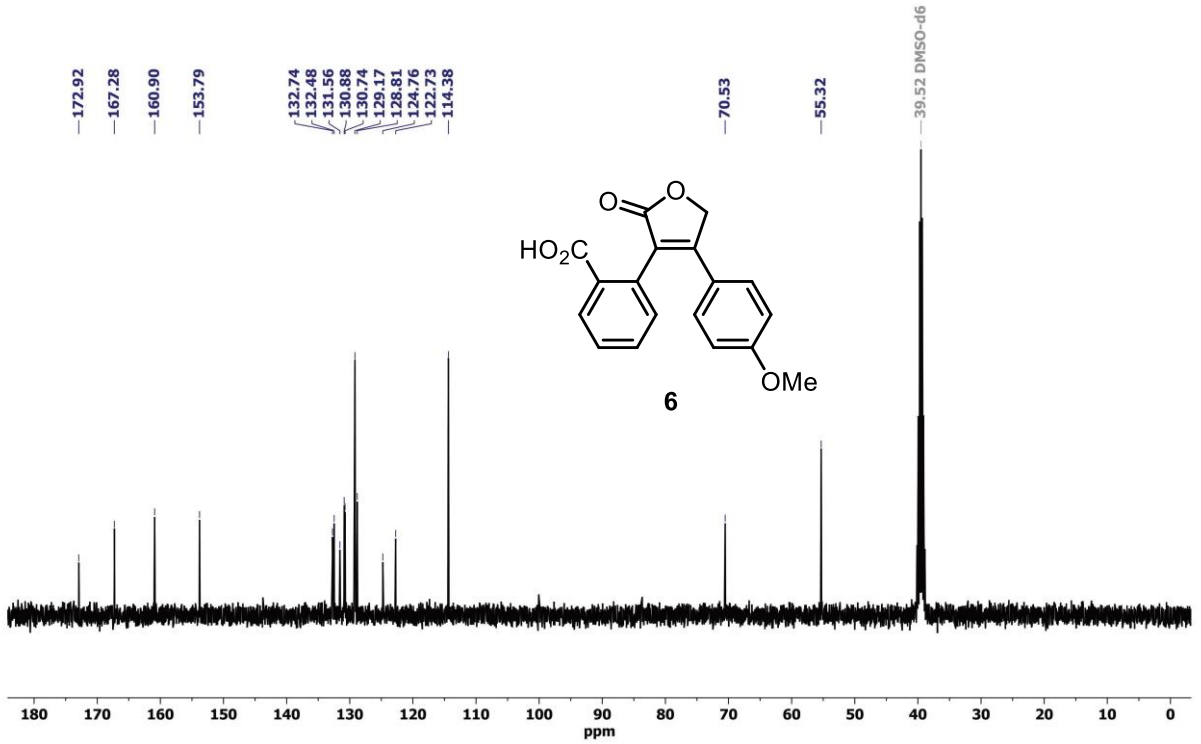
^{13}C{^{1}H} NMR spectrum of **4** in $CDCl_3$



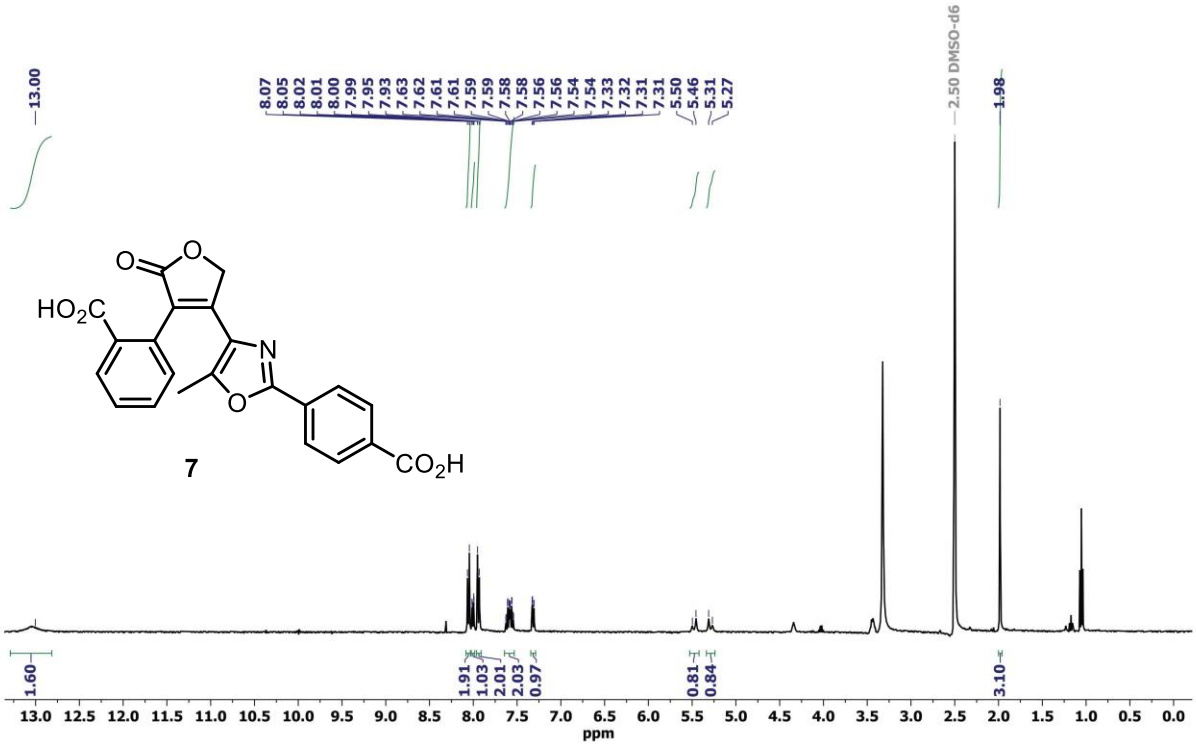
^{1}H NMR spectrum of **6** in DMSO-d_6



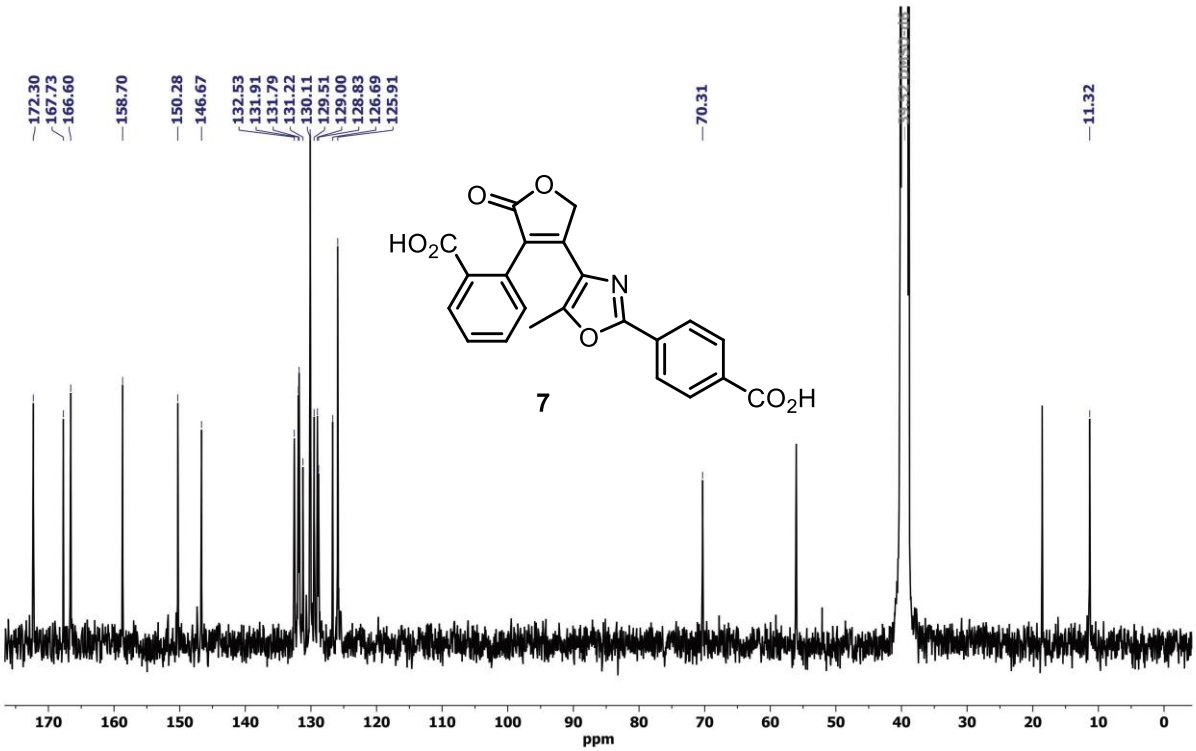
^{13}C{^{1}H} NMR spectrum of **6** in DMSO-d_6



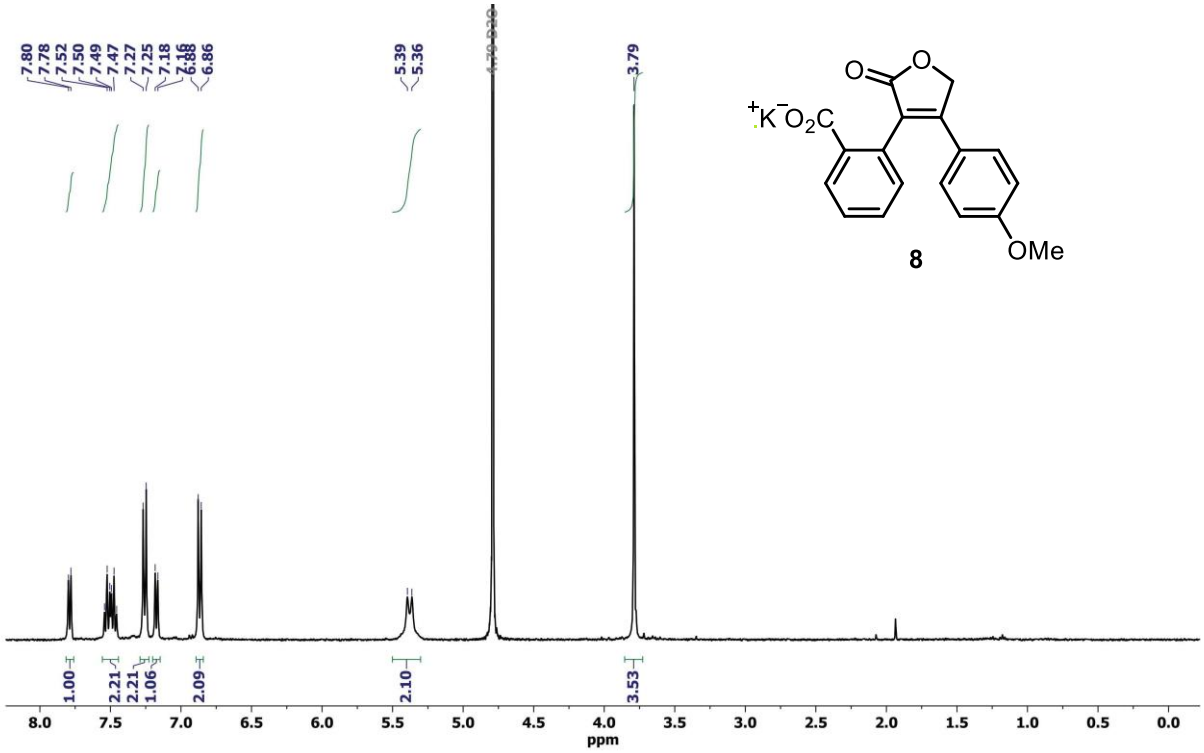
^{1}H NMR spectrum of **7** in DMSO-d_6



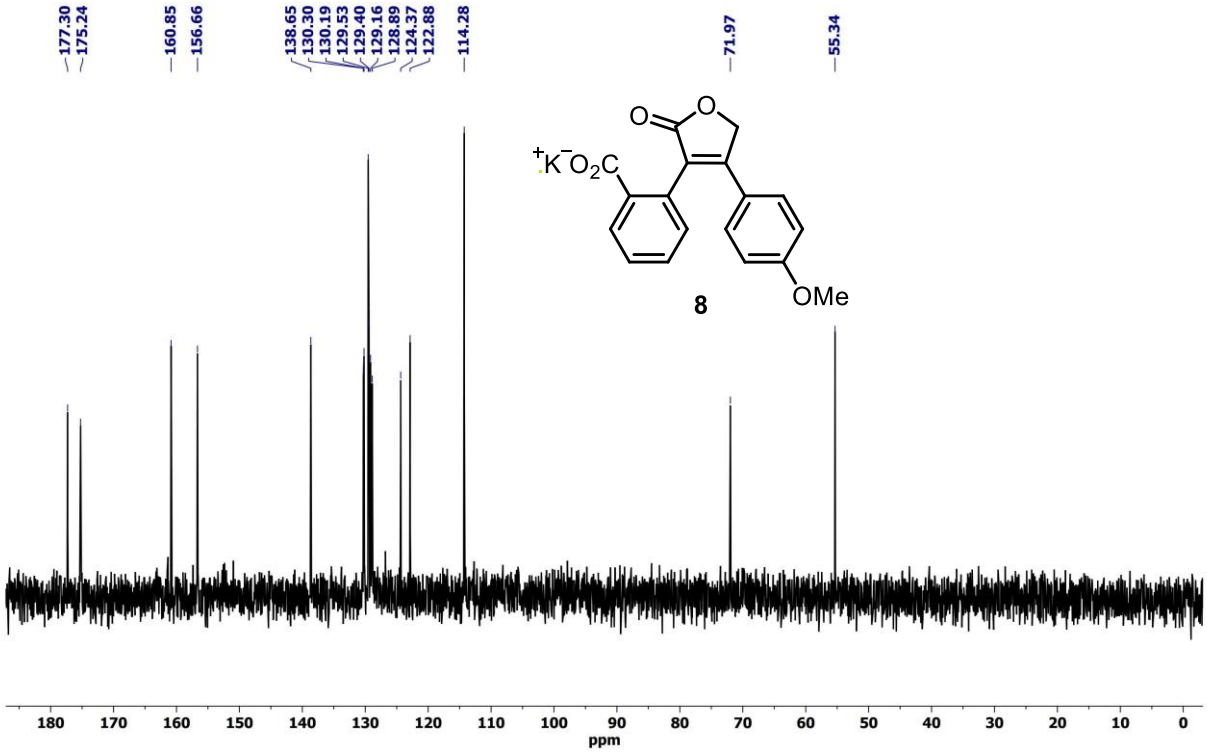
^{13}C{^{1}H} NMR spectrum of **7** in DMSO-d_6



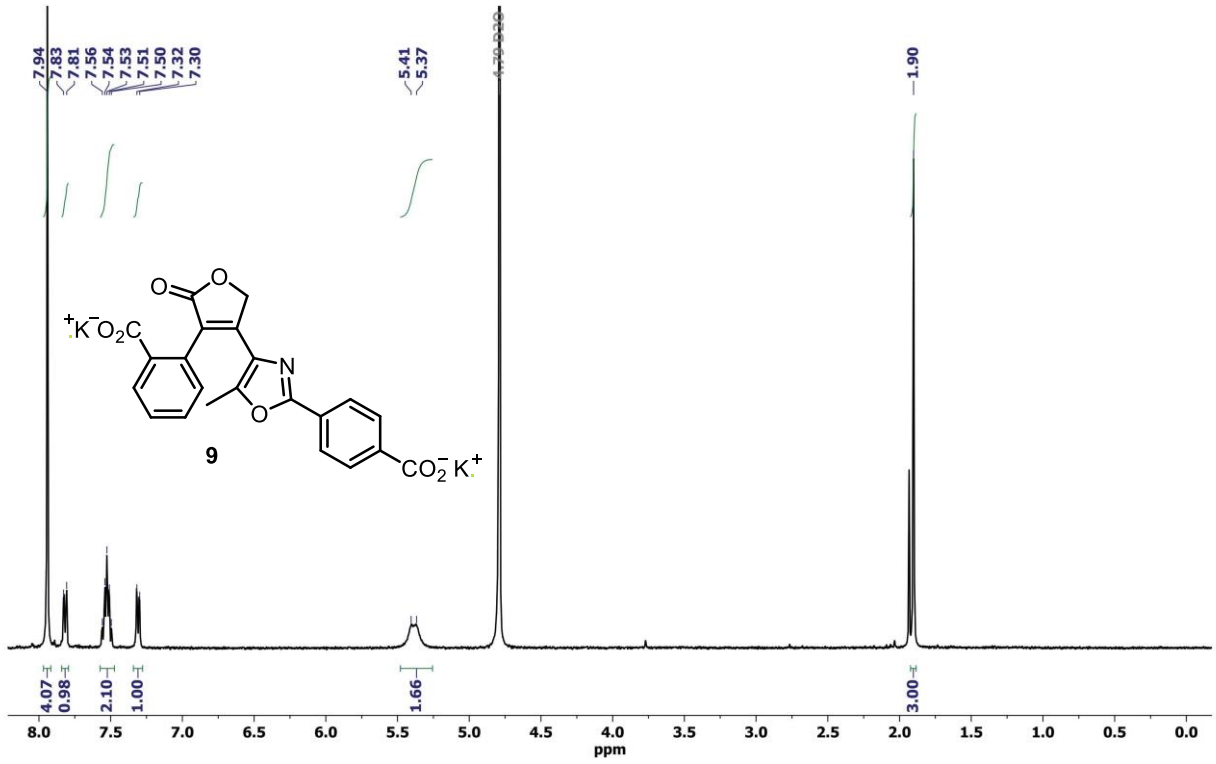
^{1}H NMR spectrum of **8** in D_2O



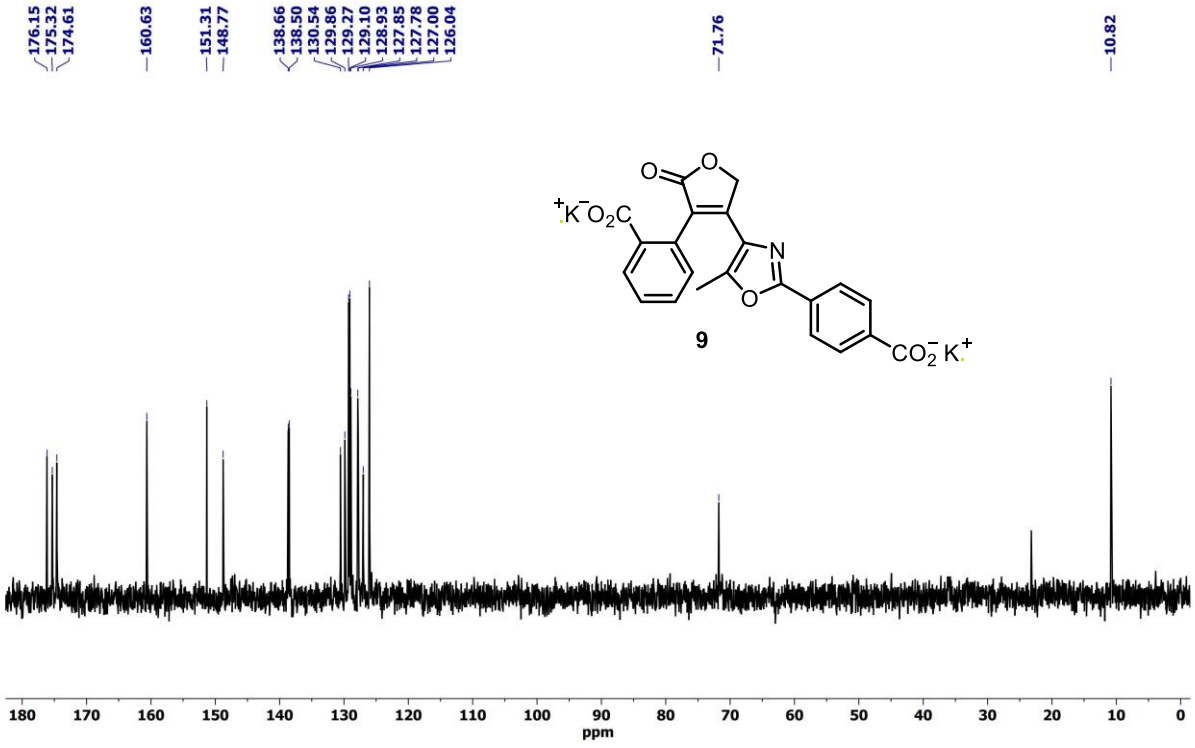
^{13}C{^{1}H} NMR spectrum of **8** in D_2O



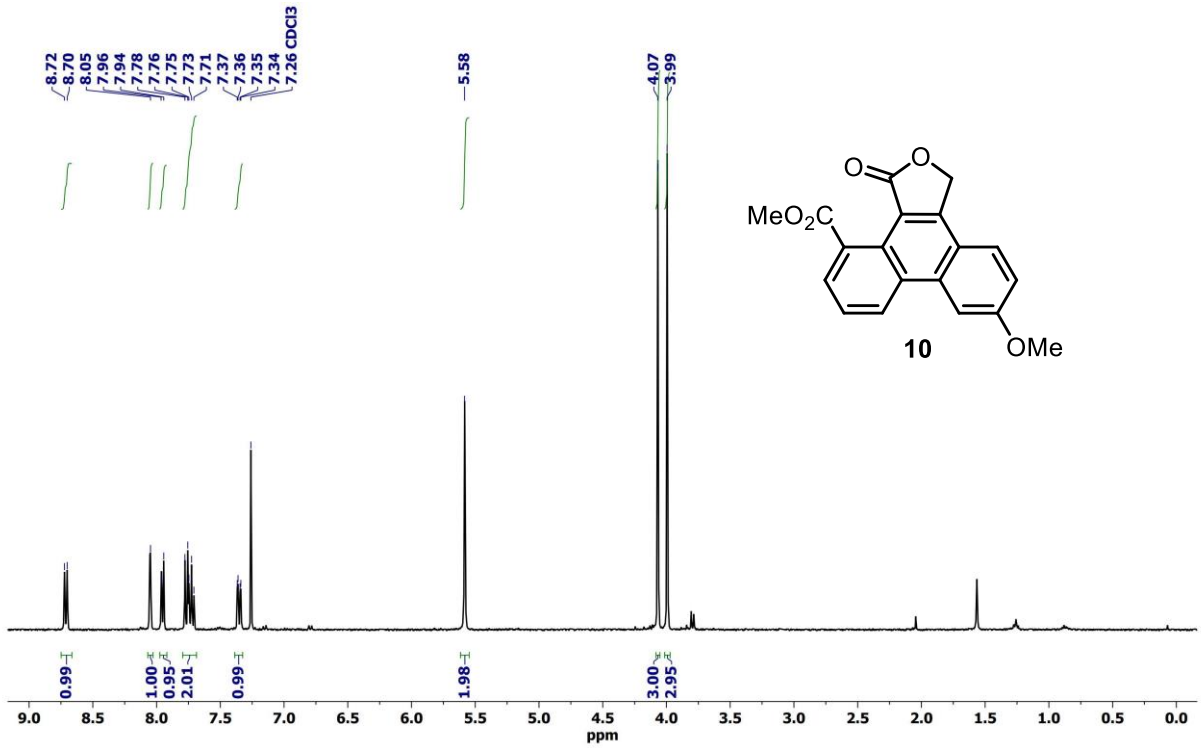
^{1}H NMR spectrum of **9** in D_2O



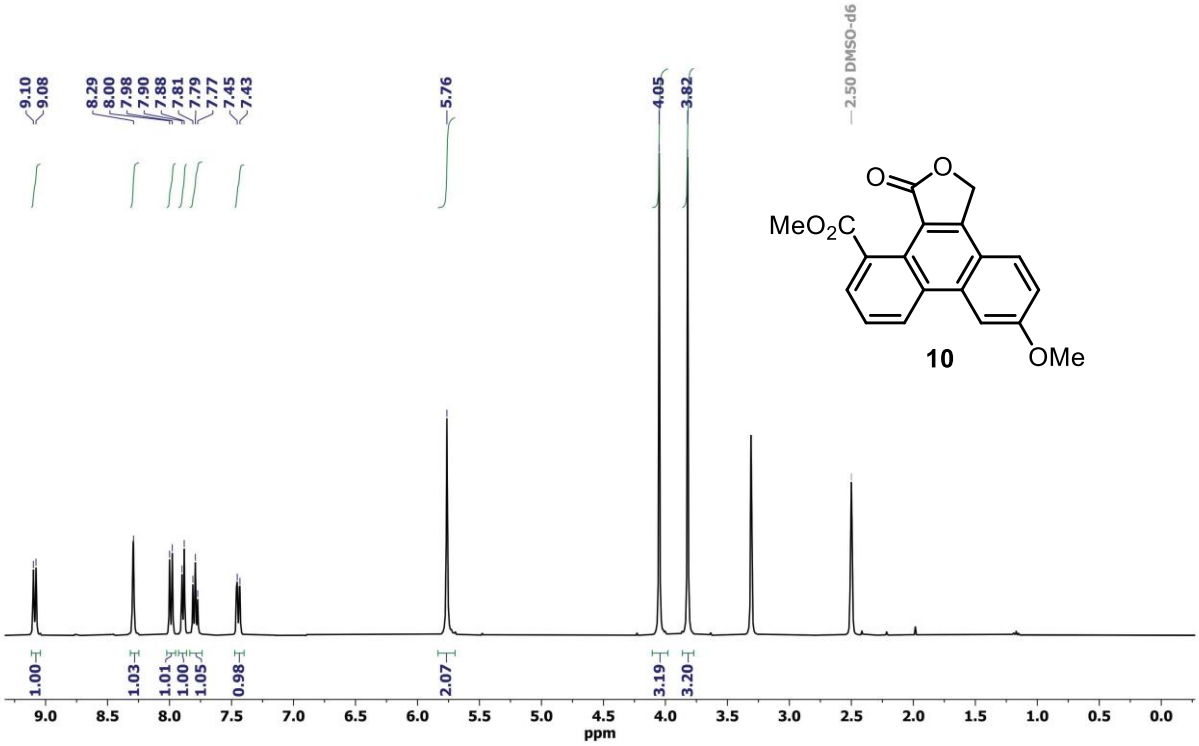
^{13}C{^{1}H} NMR spectrum of **9** in D_2O



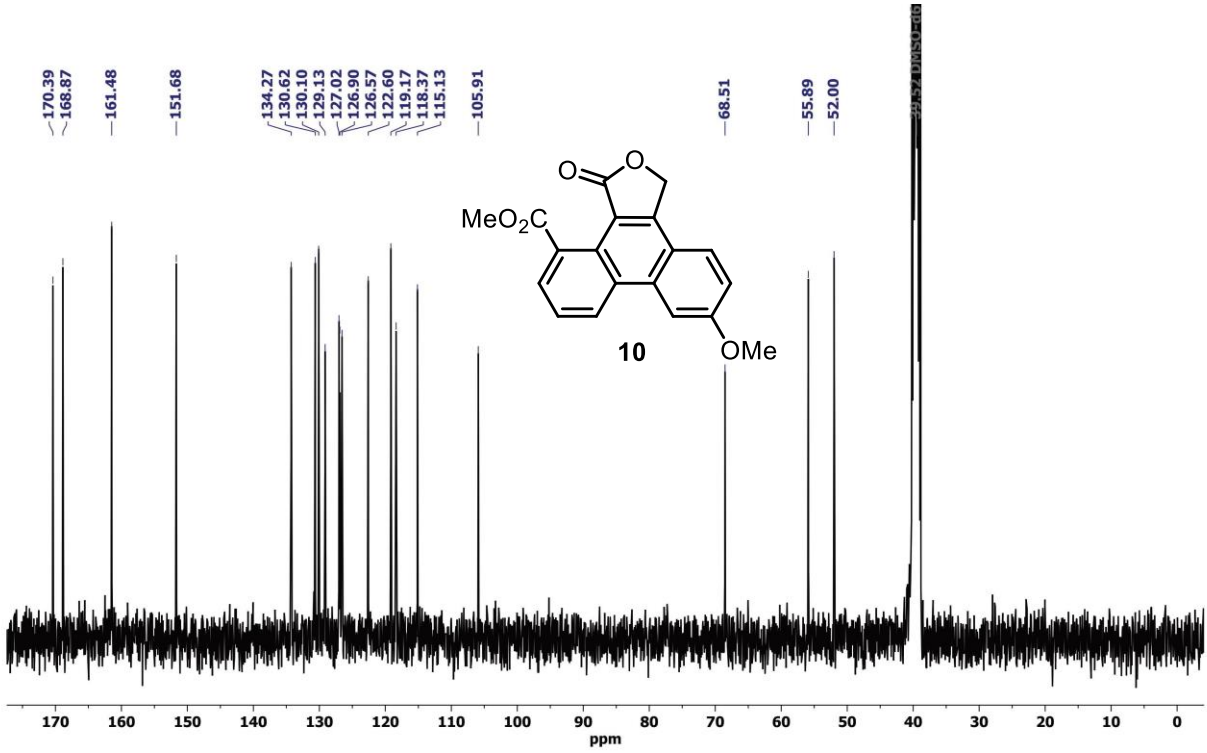
^{1}H NMR spectrum of **10** in $CDCl_3$



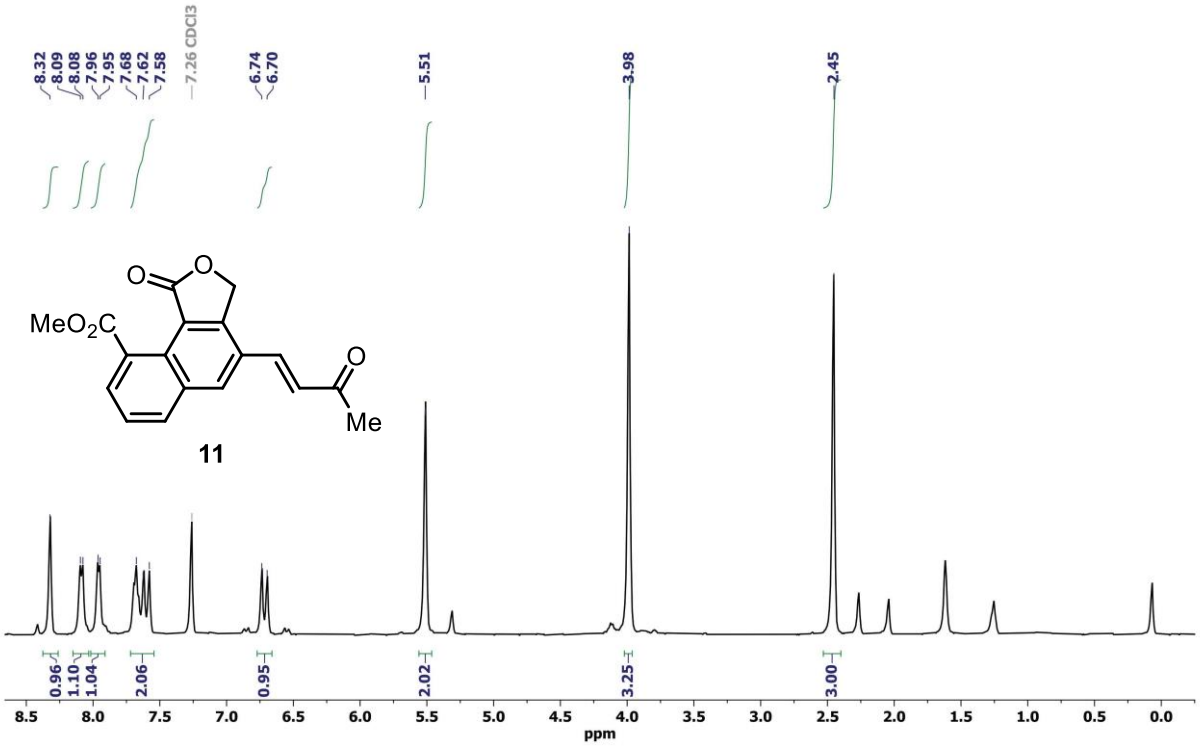
^{1}H NMR spectrum of **10** in DMSO-d_6



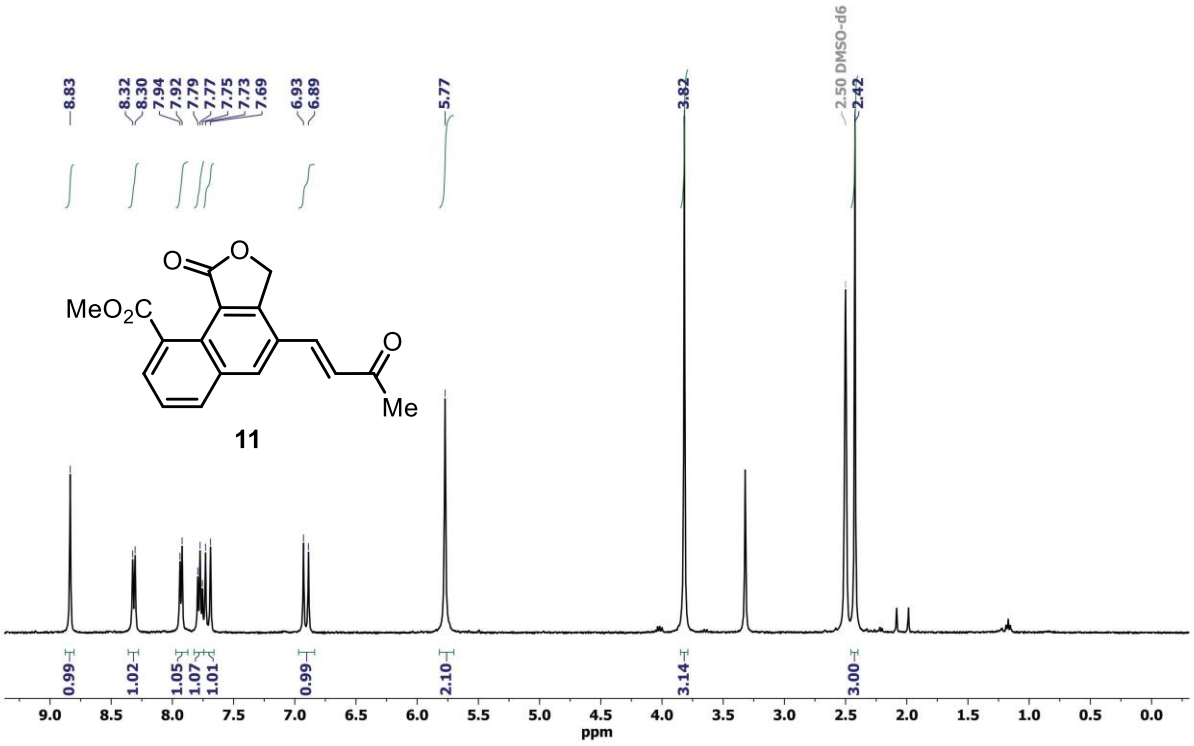
$^{13}C\{^{1}H\}$ NMR spectrum of **10** in DMSO-d_6



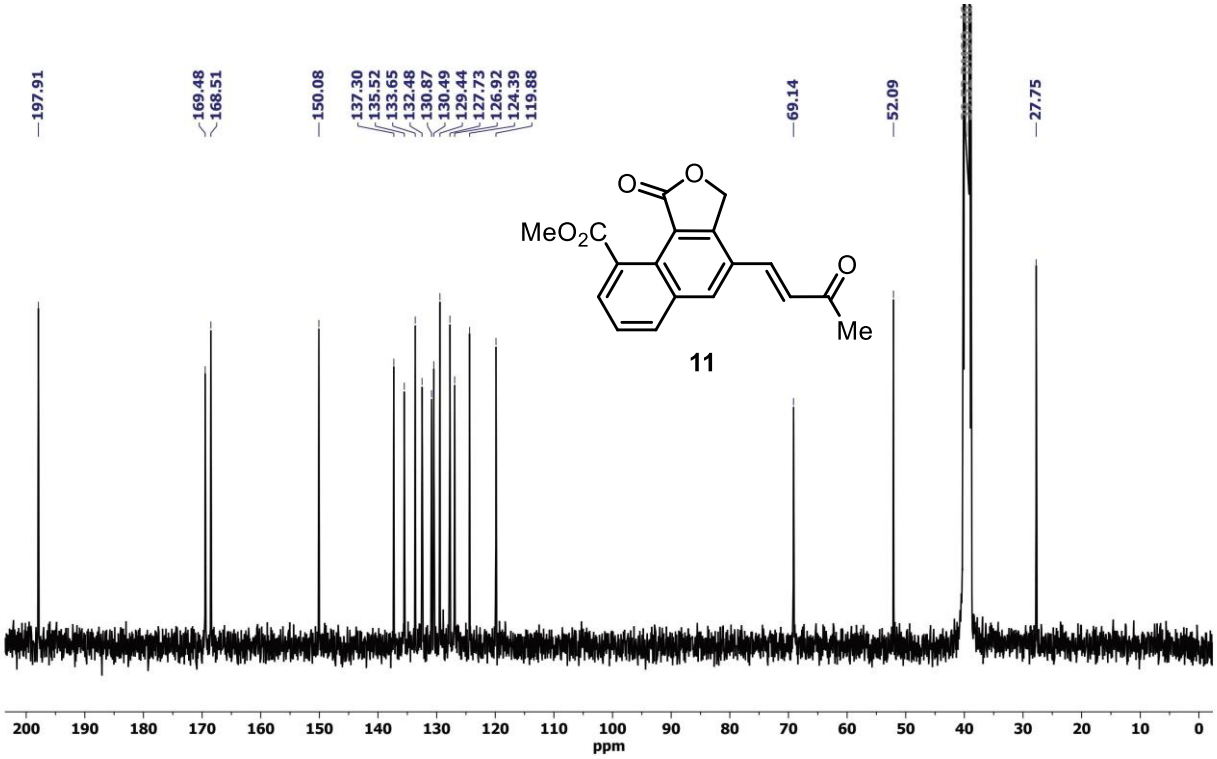
^{1}H NMR spectrum of **11** in $CDCl_3$



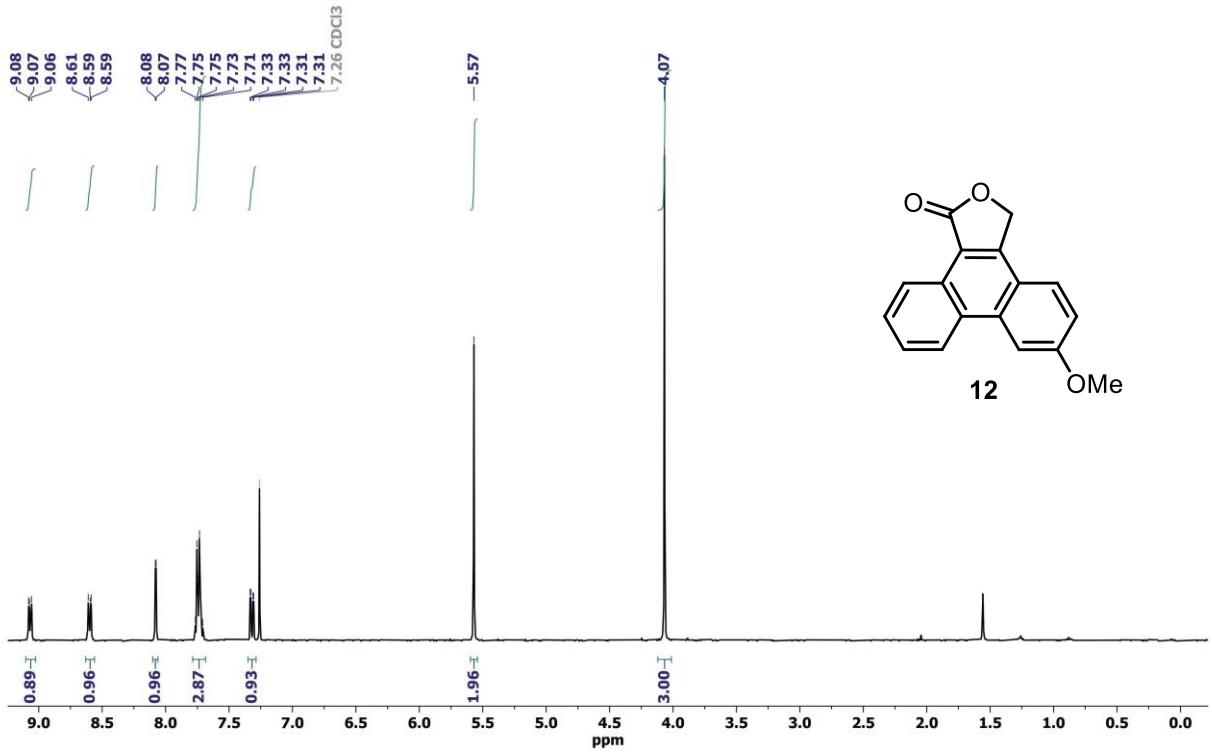
^{1}H NMR spectrum of **11** in DMSO-d_6



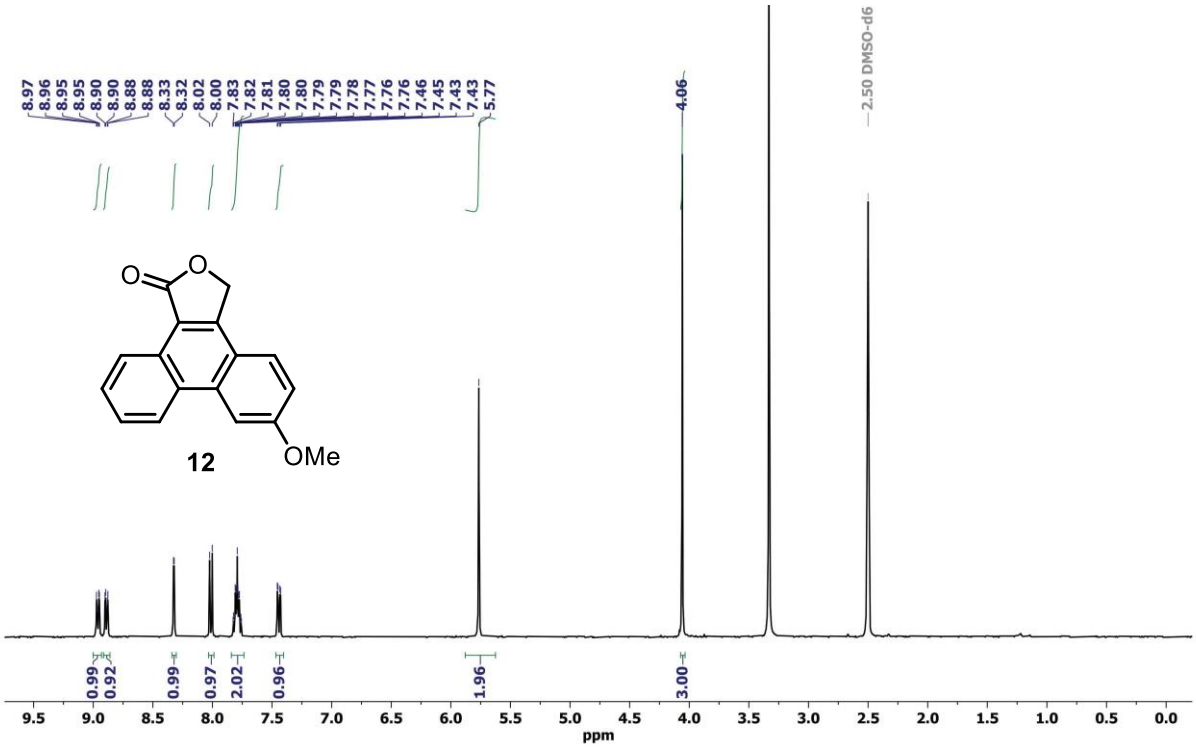
$^{13}C\{^{1}H\}$ NMR spectrum of **11** in DMSO-d_6



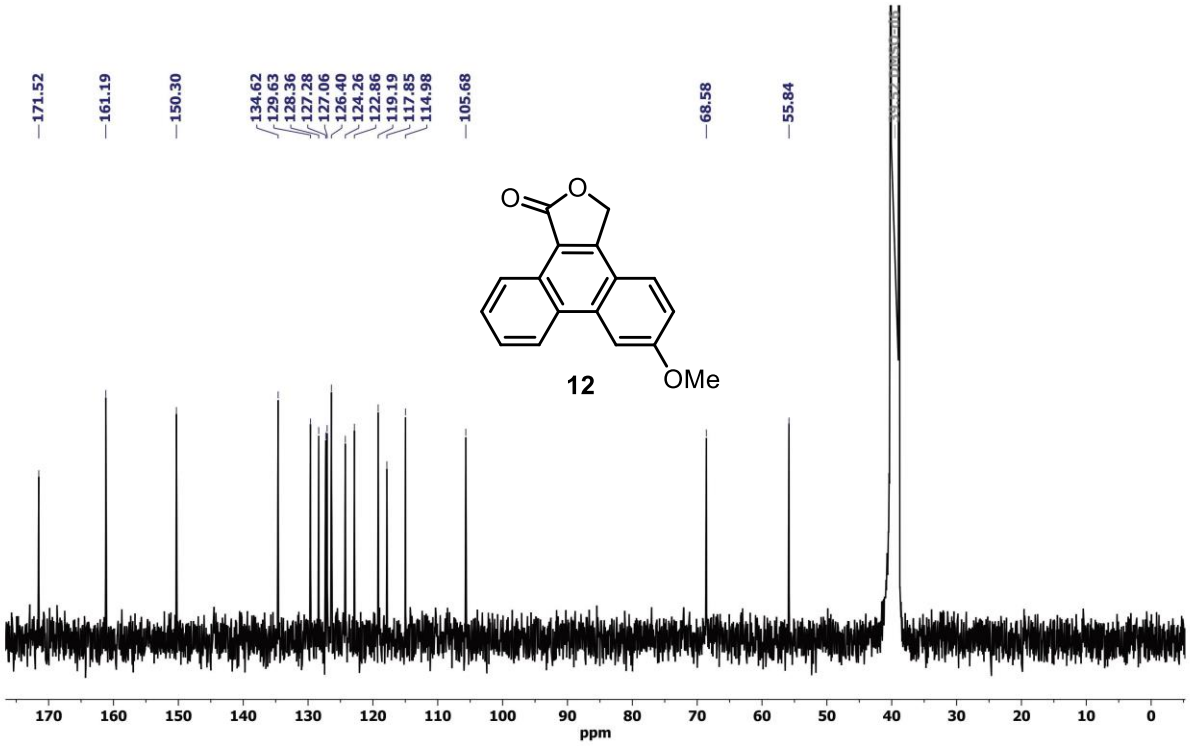
^{1}H NMR spectrum of **12** in $CDCl_3$



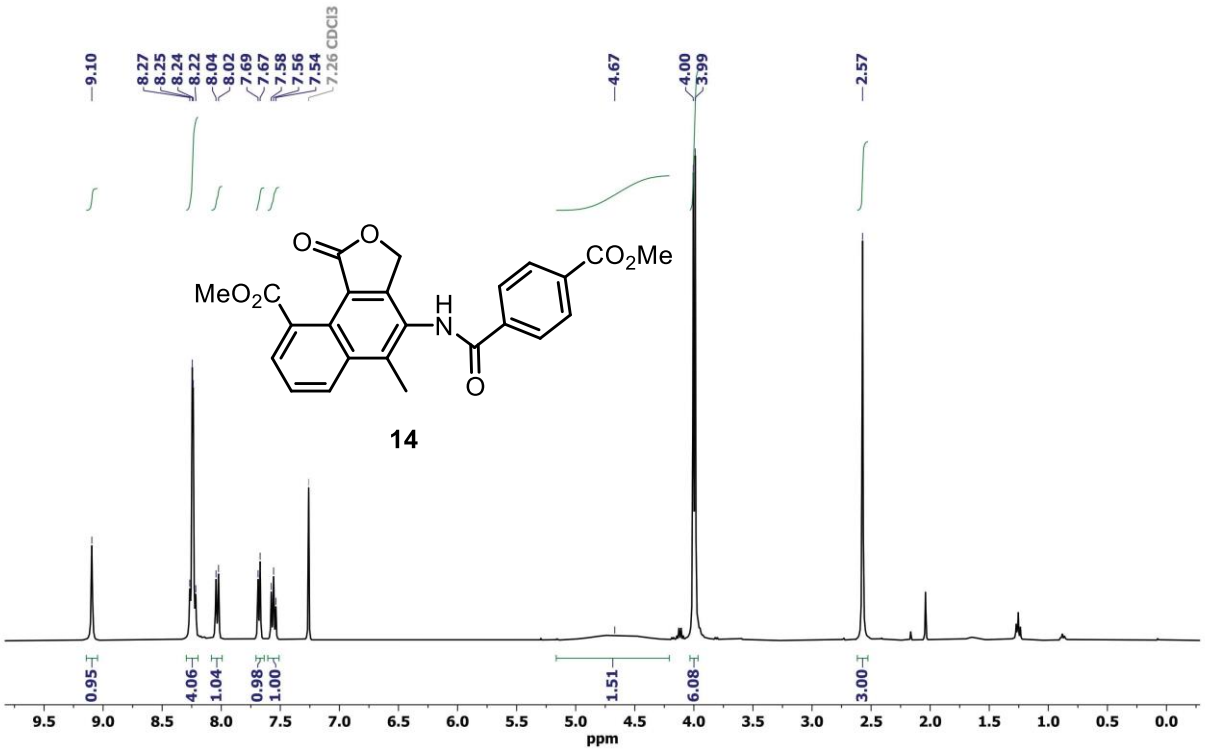
^{1}H NMR spectrum of **12** in DMSO-d_6



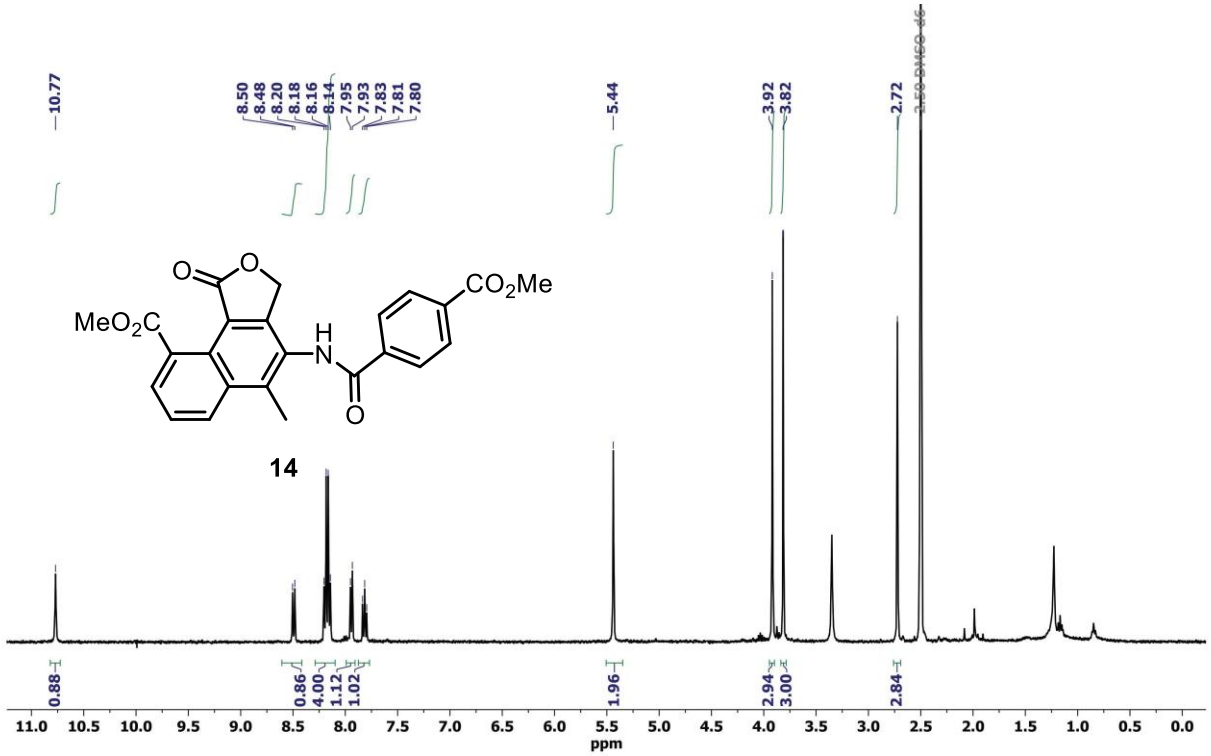
$^{13}C\{^{1}H\}$ NMR spectrum of **12** in DMSO-d_6



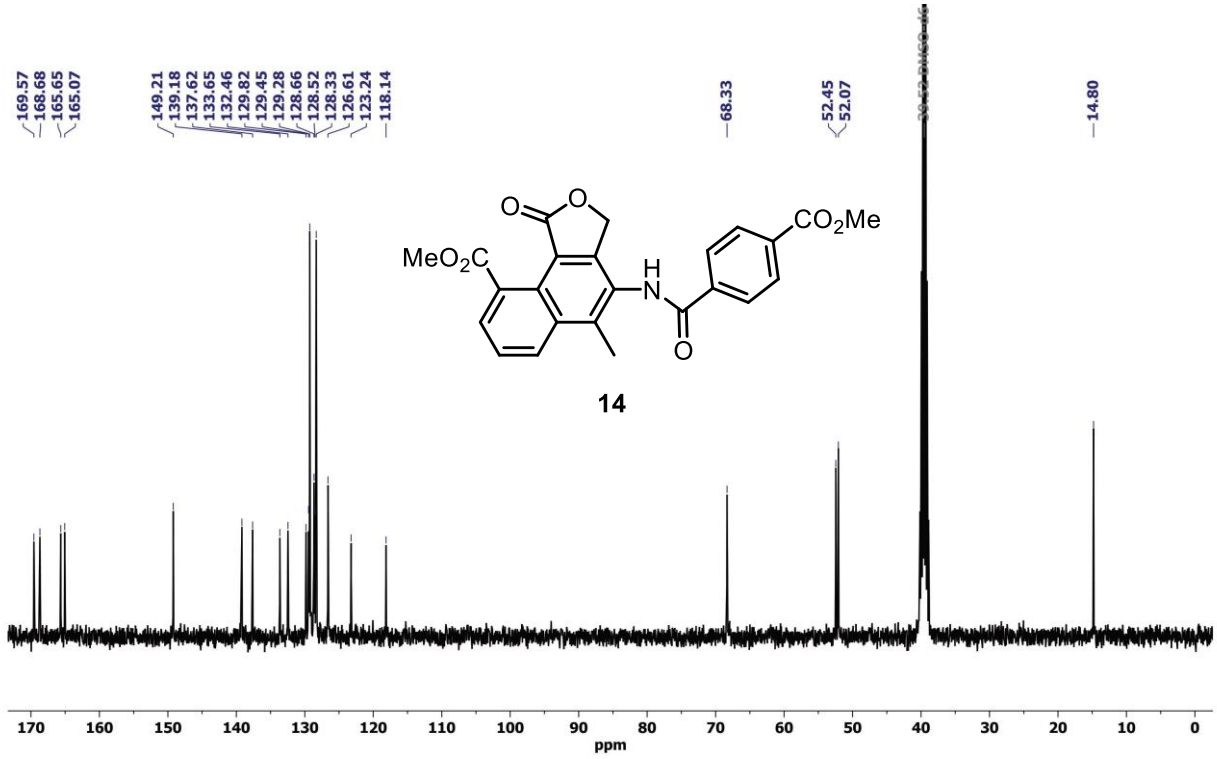
^{1}H NMR spectrum of **14** in $CDCl_3$



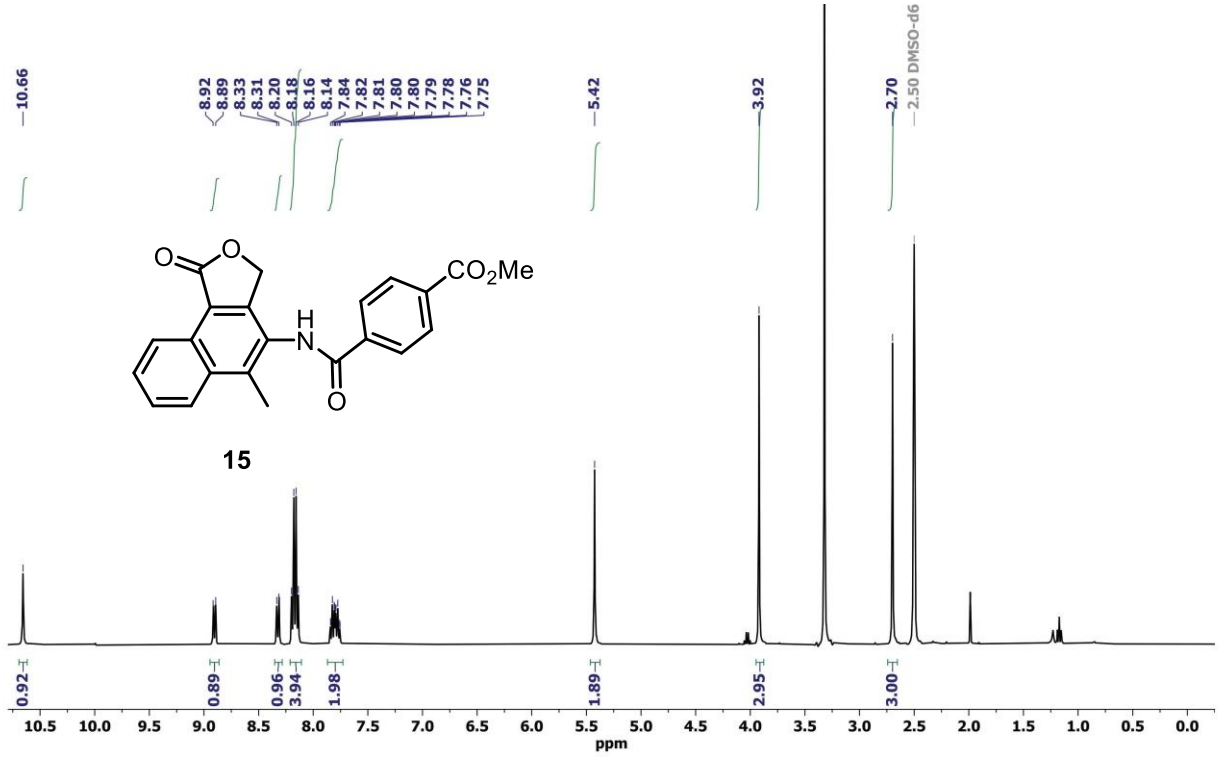
^{1}H NMR spectrum of **14** in DMSO-d_6



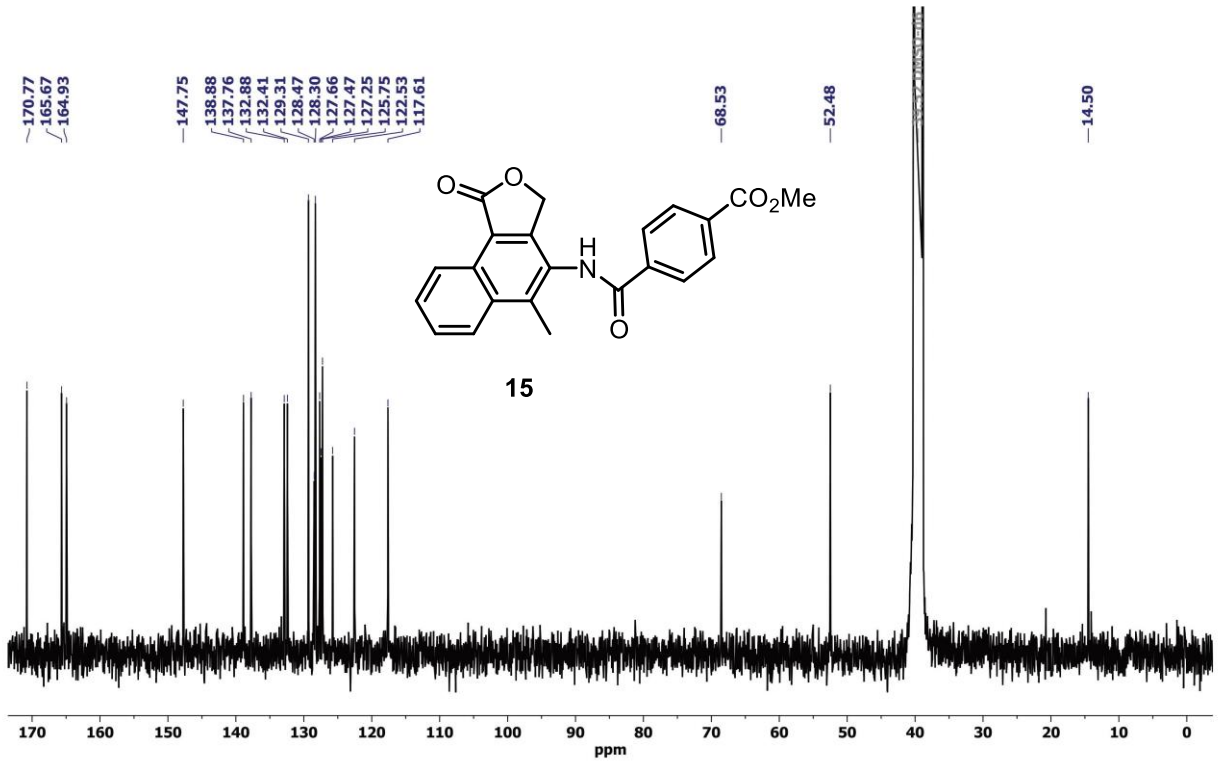
$^{13}C\{^{1}H\}$ NMR spectrum of **14** in DMSO-d_6



^{1}H NMR spectrum of **15** in DMSO-d_6

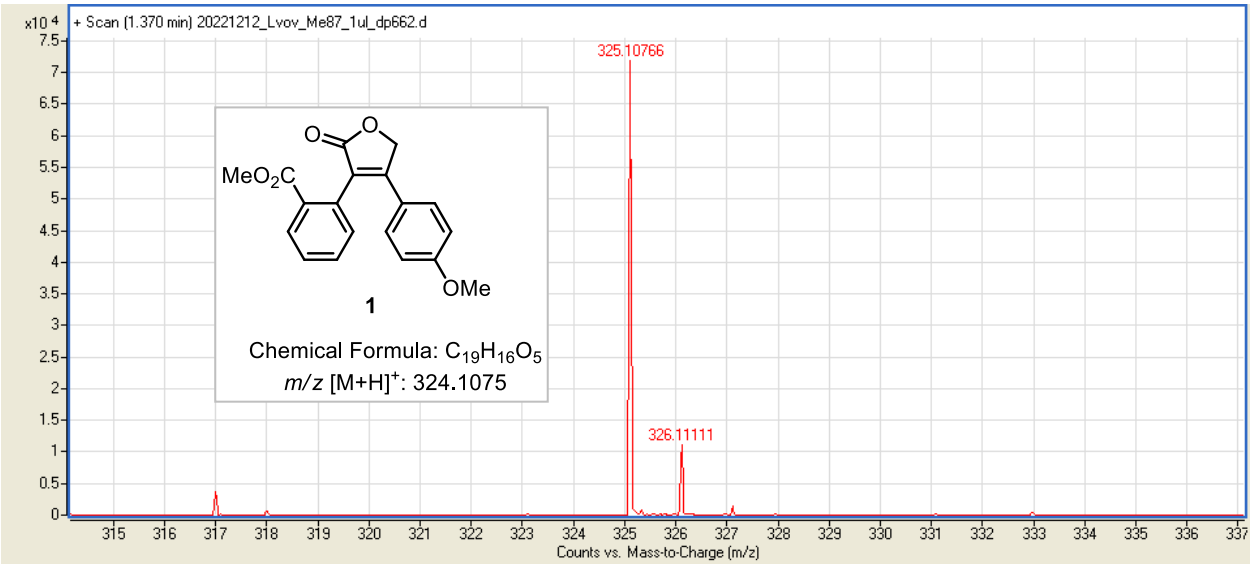


^{13}C{^{1}H} NMR spectrum of **15** in DMSO-d_6

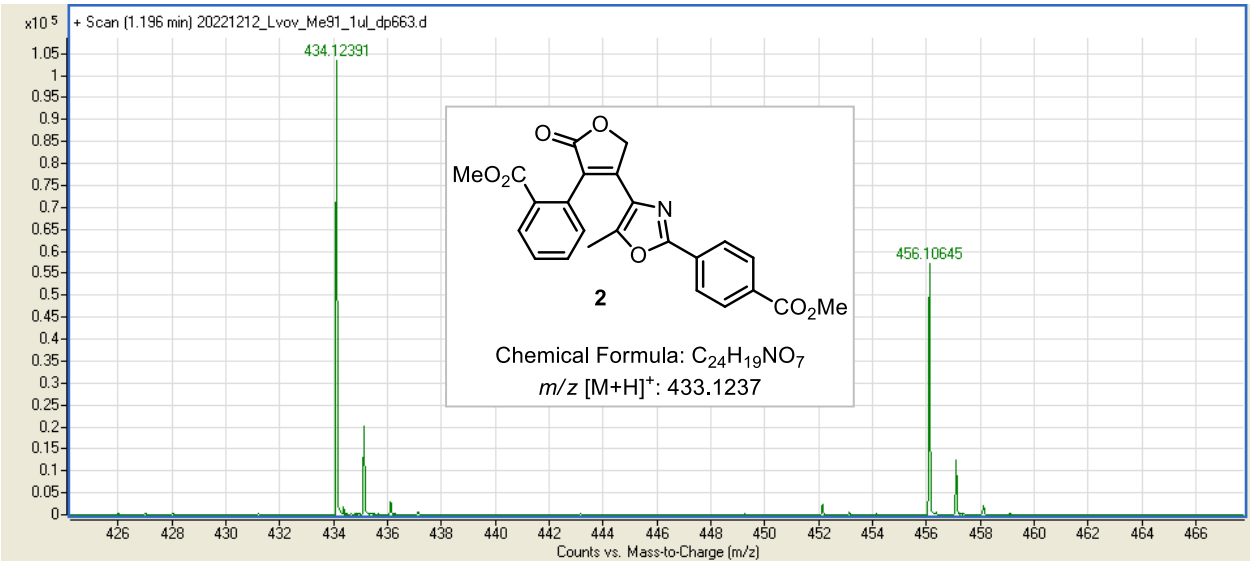


VI. Copies of HRMS spectra

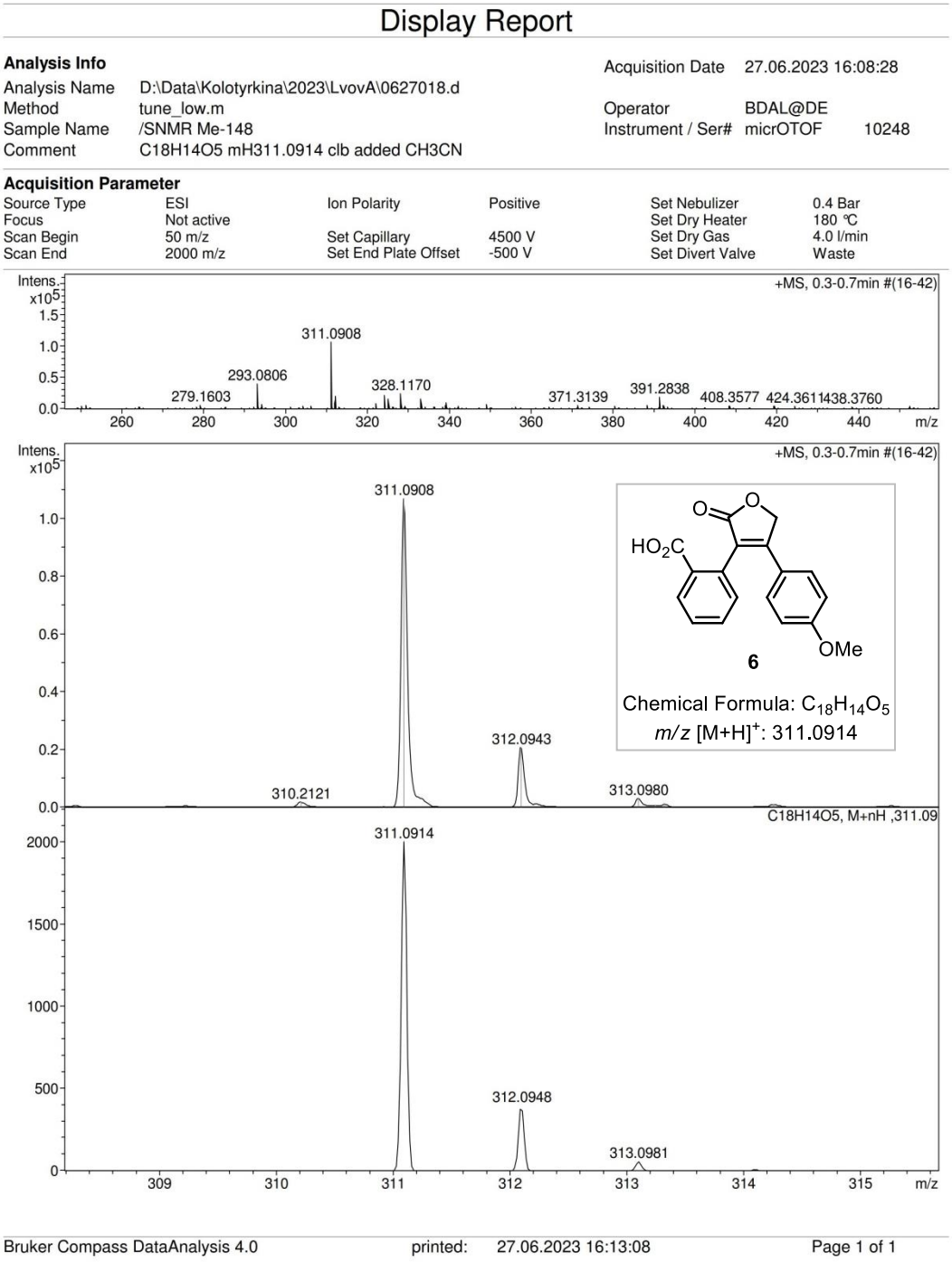
HRMS spectrum of **1**



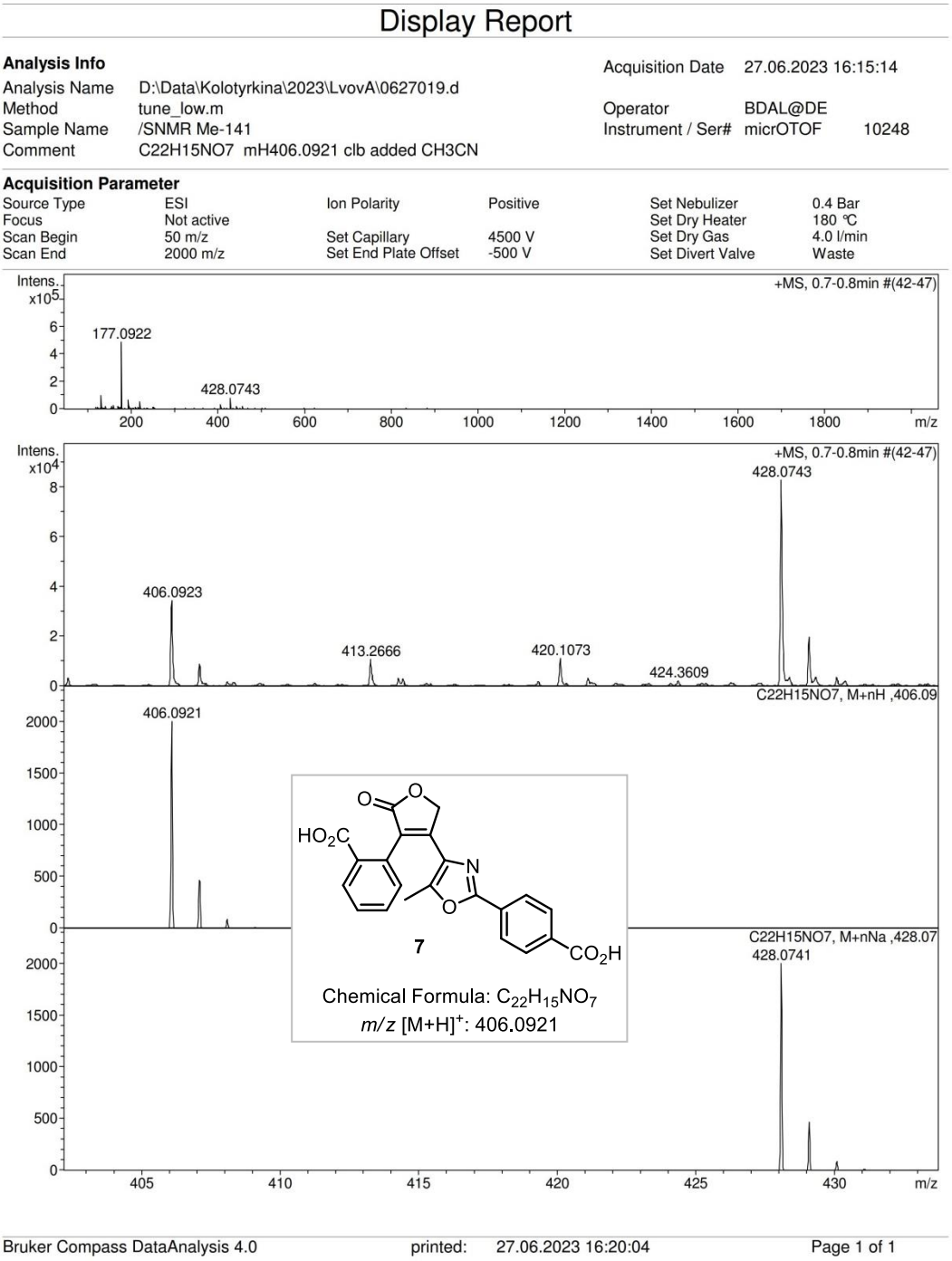
HRMS spectrum of **2**



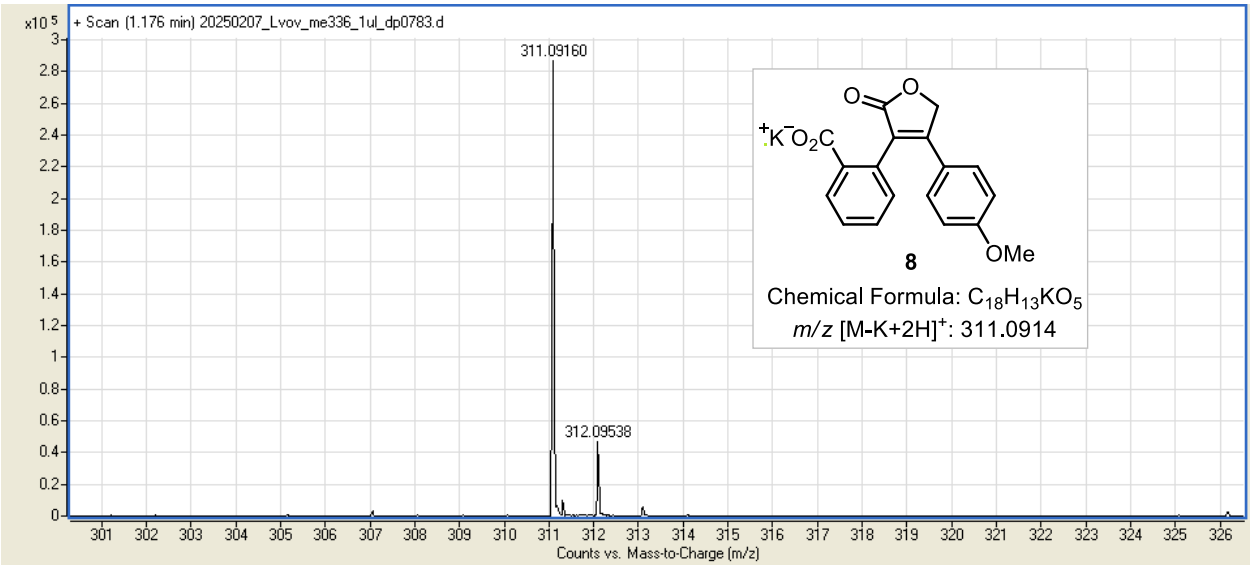
HRMS spectrum of **6**



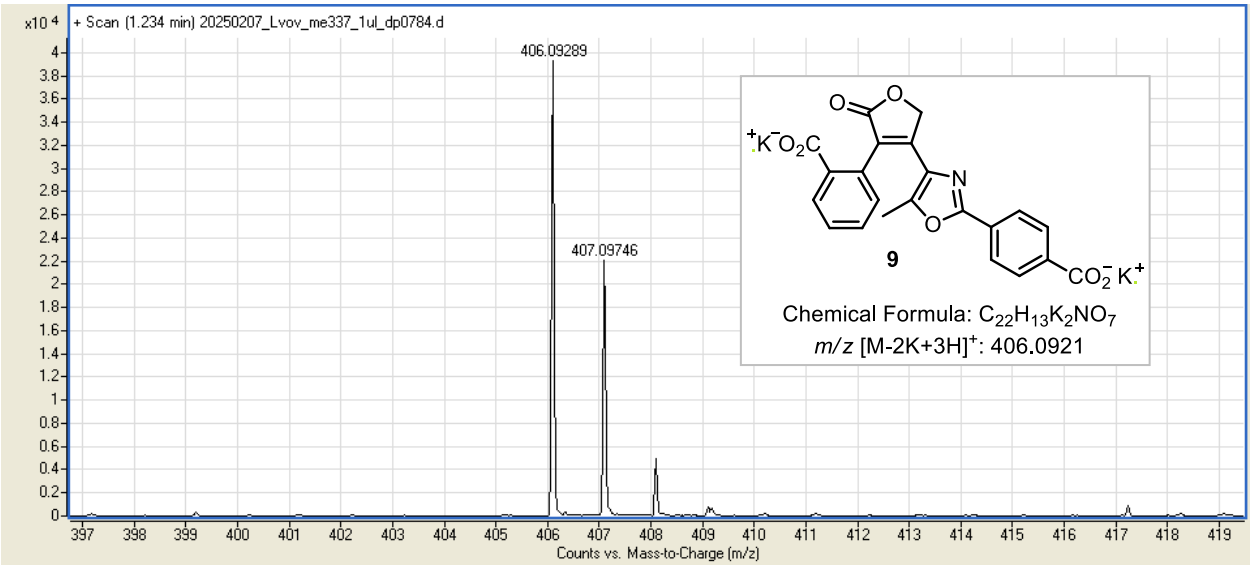
HRMS spectrum of **7**



HRMS spectrum of **8**



HRMS spectrum of **9**



HRMS spectrum of **10**

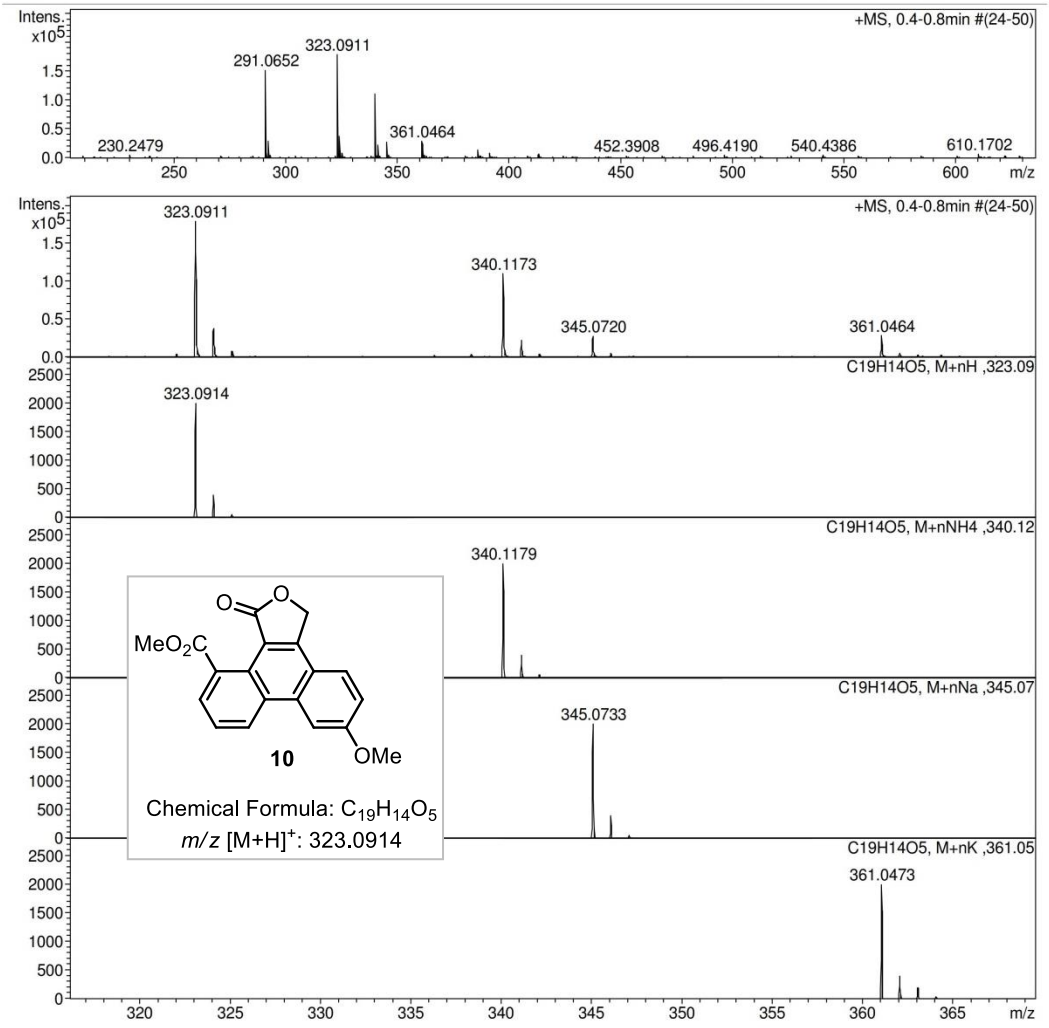
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2023\LvovA\0627024.d	Acquisition Date	27.06.2023 16:42:54
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/SNMR Me-105a-2	Instrument / Ser#	micrOTOF 10248
Comment	C19H14O5 mH323.0914 clb added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 27.06.2023 16:46:36 Page 1 of 1

HRMS spectrum of **11**

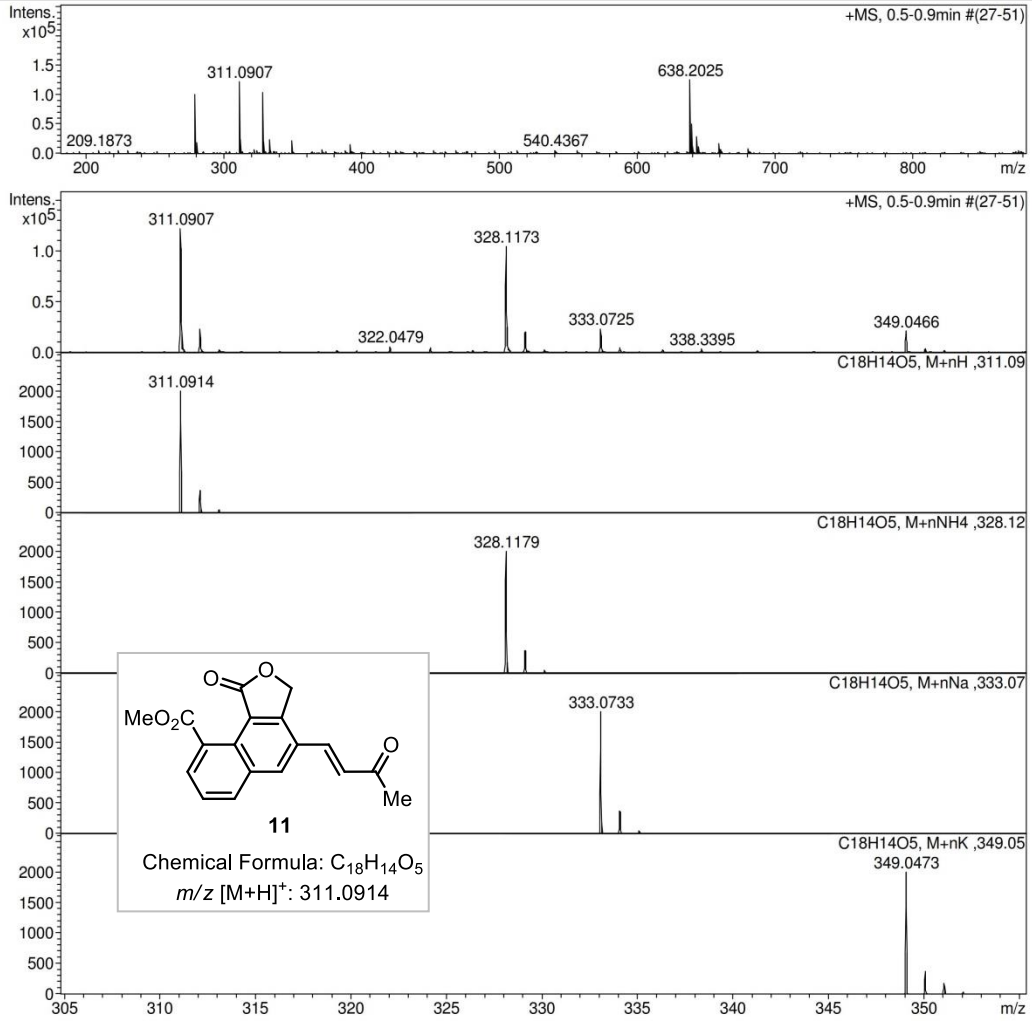
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2023\LvovA\0627020.d	Acquisition Date	27.06.2023 16:21:51
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/SNMR Me-105a-3	Instrument / Ser#	micrOTOF 10248
Comment	C18H14O5 mH311.0914 clb added CH3CN		

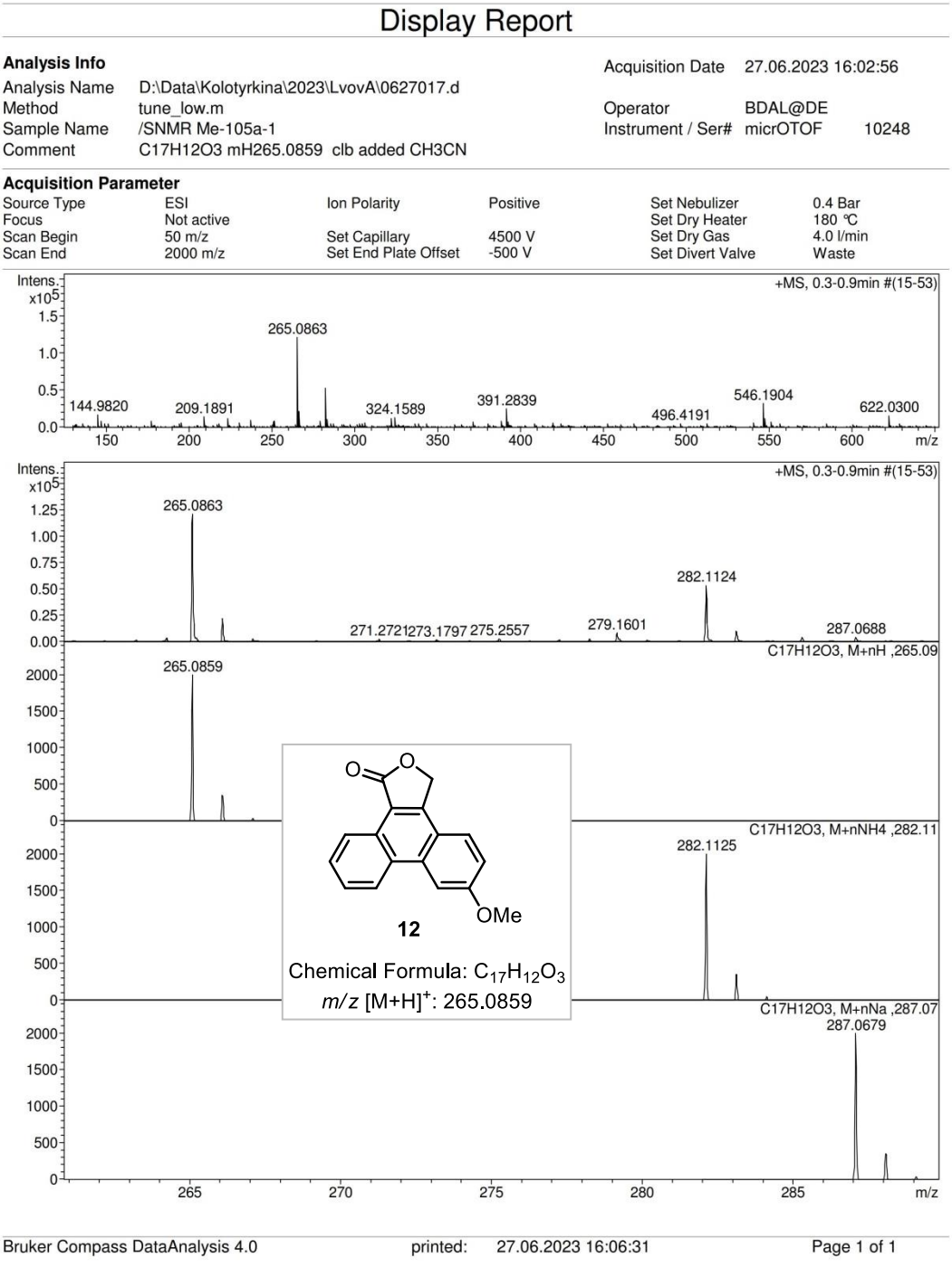
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

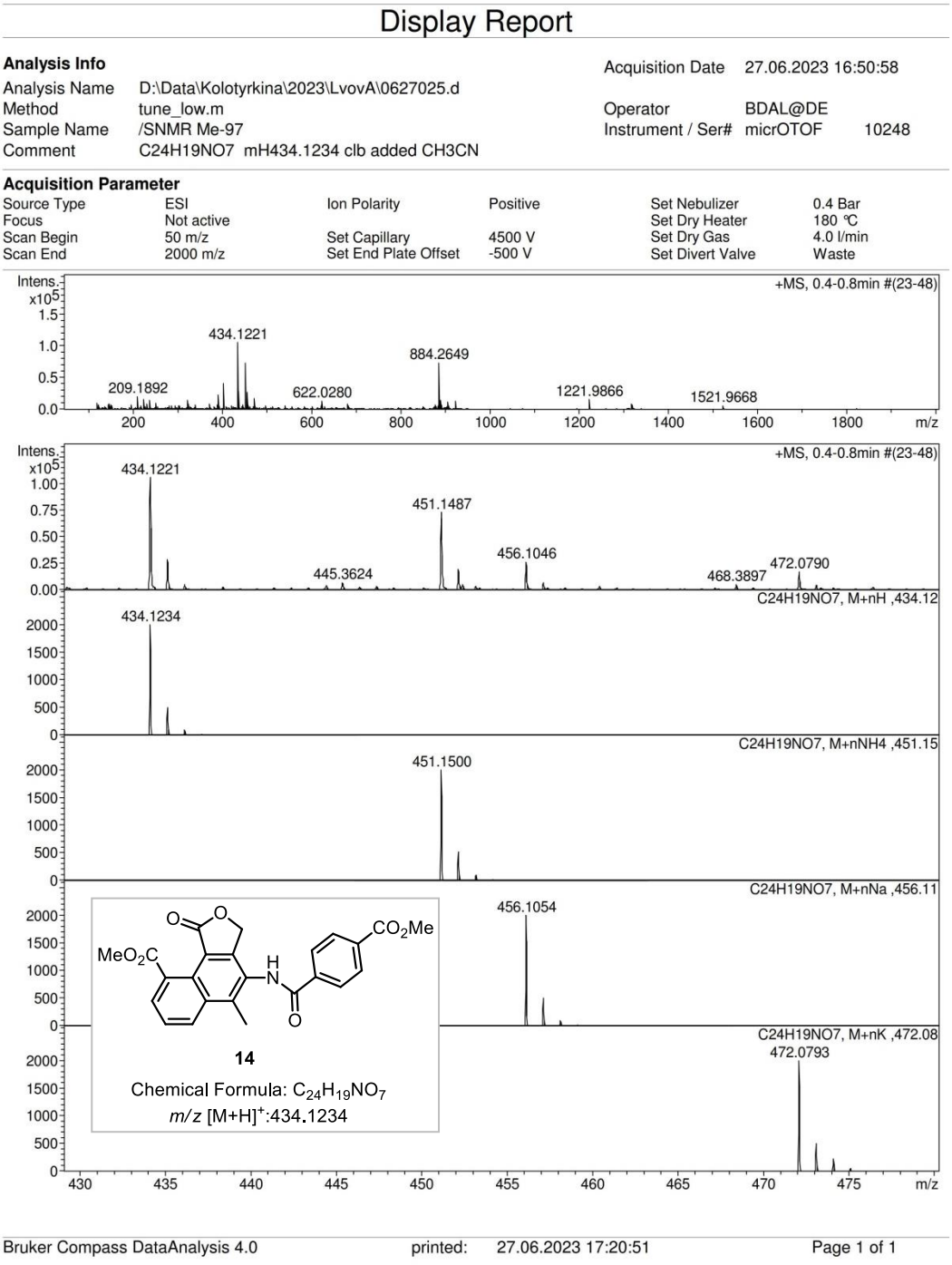


Bruker Compass DataAnalysis 4.0 printed: 27.06.2023 16:25:02 Page 1 of 1

HRMS spectrum of **12**



HRMS spectrum of **14**



HRMS spectrum of **15**