

3-Acyl-2-furylthiochromones: a new family of compounds with photoinduced fluorescence

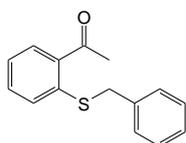
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NMR spectra were recorded on a Bruker AM-300 (300 MHz) instrument in DMSO- d_6 or $CDCl_3$. EI mass spectra were measured on a Finnigan MAT INCOS 50 instrument using a direct inlet system; the ionization energy was 70 eV. High resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurements were done in a positive ion mode (interface capillary voltage – 4500 V); mass range from m/z 50 to m/z 3000; internal calibration was done with ESI Tuning Mix, Agilent. A syringe injection was used for solutions in acetonitrile (flow rate 3 μ L/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. Melting points were measured on a Boetius hot-stage apparatus (uncorrected). The reaction mixtures were analyzed, and the purity of all products was checked by TLC on Silica gel 60 F₂₅₄ plates (Merck).

The spectral-kinetic absorption and fluorescent characteristics of dilute non-deoxygenated toluene solution of the starting compounds were measured on a spectrophotometer Cary 50 bio (Varian) and a spectrofluorimeter Cary Eclipse (Varian), respectively. Absorption measurements were carried out in cuvettes of 2 mm thick ($C = 2 \cdot 10^{-4}$ M). Spectrophotometric cells of 10 mm thick were used for fluorescence investigations ($C = 4 \cdot 10^{-5}$ M).

To obtain photoproducts **B**, solutions of chromones in toluene were irradiated directly in a spectrophotometric cell of 2 mm thick with the light from a high-pressure mercury–xenon lamp L8253 of the illuminator LC-4 (Hamamatsu) through the UFS-1 glass light filter or without any filters.

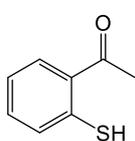
***o*-(Benzylthio)acetophenone.** Benzylmercaptan (5.00 g, 40.3 mmol), *o*-nitroacetophenone (6.65 g, 40.3 mmol) were dissolved in DMF (150 ml).



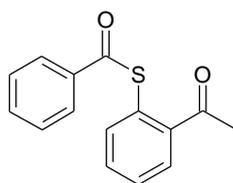
Lithium hydroxide monohydrate (5.00 g, 208.3 mmol) was added and the mixture was stirred at rt for 12 h. The mixture was poured into ice, and

precipitate formed was collected by filtration, washed with water and ethanol, dried at rt. Yield 7.54 g (77 %).

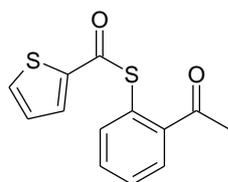
***o*-Mercaptoacetophenone.** *o*-(Benzylthio)acetophenone (7.54 g, 29.4 mmol) was dissolved in anhydrous toluene (120 ml). Anhydrous aluminium trichloride (7.30 g, 54.9 mmol) was added to the mixture, and the suspension was stirred in inert atmosphere for 24 h (rt). The mixture was washed with water, the product was extracted with NaOH (10% aq. solution), the aqueous extracts were washed with ether, and then acidified with HCl solution to pH ~ 5, the product was extracted with ether. The organic phase was washed with water, dried with anhydrous Na₂SO₄, the solvent was evaporated. Yield 3.68 g (82%).



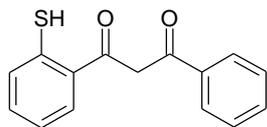
***S*-(2-Acetylphenyl) benzothioate (2a).** *o*-Mercaptoacetophenone (3.68 g, 24.2 mmol) and benzoyl chloride (3.76 g, 3.4 ml, 26.6 mmol) were dissolved in CH₂Cl₂ (15 ml). Triethylamine (2.7 g, 3.7 ml, 26.7 mmol) was added dropwise and the mixture was stirred at rt for 1 h. The mixture was washed 2 times with water, dried with anhydrous Na₂SO₄, concentrated under reduced pressure. The product was purified by column chromatography (hexane–ethyl acetate = 5:1) to yield 5.44 g (88%) of a reddish oil.



***S*-(2-Acetylphenyl) thiophene-2-carbothioate (2b)** was obtained similarly to **2a**. Yield (58%). ¹H NMR (300 MHz, CDCl₃) δ 7.94 (d, *J* = 3.4 Hz, 1H), 7.75 – 7.61 (m, 3H), 7.57 – 7.47 (m, 2H), 7.22 – 7.07 (m, 1H), 2.62 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 200.76, 181.42, 143.51, 141.15, 137.06, 133.49, 131.95, 131.17, 129.54, 128.49, 128.08, 125.13, 29.39. HRMS: found *m/z* 263.0192; calculated for C₁₃H₁₀O₂S₂ [M+H]⁺ 263.0195; found *m/z* 285.0012; calculated for C₁₃H₁₀O₂S₂ [M+Na]⁺ 285.0014; found *m/z* 300.9756; calculated for C₁₃H₁₀O₂S₂ [M+K]⁺ 300.9754.

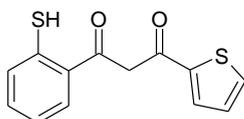


1-(2-Mercaptophenyl)-3-phenylpropane-1,3-dione (3a). *S*-(2-acetylphenyl) benzothioate (**2a**) (2.72 g, 10.63 mmol) was dissolved in anhydrous THF (40 ml) in inert atmosphere. The mixture was cooled to –15 °C and then LDA (2 M in toluene, 10.6 ml, 21.25 mmol) was added. The solution was stirred for 1 h between –15 and 0 °C and then THF was evaporated under reduced pressure. The mixture was acidified to pH = 7, extracted with chloroform, the organic phase was washed with water and dried with anhydrous Na₂SO₄. The solvent was evaporated and the product was purified by flash chromatography (hexane–ethyl acetate = 5:1) to yield 1.7 g



(63%) of **2a** as a brown solid. M. p. 115–117 °C (lit. 116–118 °C) [J. I. Lee, M. J. Kim, *Bull. Korean Chem. Soc.*, 2011, **32**, 1383].

1-(2-Mercaptophenyl)-3-(2-thienyl)propane-1,3-dione (3b). *S*-(2-Acetylphenyl)



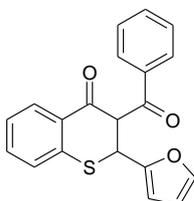
thiophene-2-carbothioate (**2b**) (2.62 g, 10 mmol) was dissolved in anhydrous THF (40 ml) in inert atmosphere. The mixture was cooled to –70 °C and then LDA (2 M in toluene, 10 ml, 20 mmol) was added. The solution was stirred for 1 h between –70 and –40 °C and then THF was

evaporated under reduced pressure. The mixture was acidified to pH 7, extracted with chloroform, the organic phase was washed with water and dried with anhydrous Na₂SO₄. The solvent was evaporated and the product was purified by flash chromatography (hexane–ethyl acetate = 5:1) to yield 0.7 g (27%) of **3b** as a pale yellow solid. M.p. 82–90 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.19 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.82 – 7.63 (m, 1H), 7.53 – 7.45 (m, 1H), 7.40 – 7.15 (m, 4H), 7.06 (dd, *J* = 5.0, 3.7 Hz, 1H), 3.47 (s, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 192.77, 147.36, 138.53, 134.03, 128.95, 127.39, 127.30, 126.26, 125.73, 124.68, 121.37, 82.78, 55.08. HRMS: found *m/z* 263.0191; calculated for C₁₃H₁₀O₂S₂ [M+H]⁺ 263.0195; found *m/z* 285.0009; calculated for C₁₃H₁₀O₂S₂ [M+Na]⁺ 285.0014; found *m/z* 300.9751; calculated for C₁₃H₁₀O₂S₂ [M+K]⁺ 300.9754.

Preparation of thiochromanones (4a–c/4'a–c) (general procedure). To a solution of 1-(2-mercaptophenyl)-3-arylpropane-1,3-dione **3a,b** (2.0 mmol) in ethanol (2 ml) furfural was added (4.0 mmol) followed by one drop of piperidine. The solution was stirred at rt until TLC showed disappearance of the starting material. After that precipitate was collected by filtration and recrystallized from ethanol.

3-Benzoyl-2-(2-furyl)thiochroman-4-one (4a). Yield 0.38 g (57%). M.p. 129–131 °C.

¹H NMR (300 MHz, CDCl₃) δ 17.21 (s, 1H), 8.14 (d, *J* = 7.5 Hz, 1H), 7.55 – 7.16 (m, 9H), 6.18 (d, *J* = 2.2 Hz, 1H), 6.05 (d, *J* = 2.9 Hz, 1H), 5.11 (s, 1H).

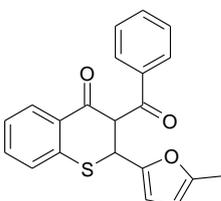


¹³C NMR (75 MHz, CDCl₃) δ 190.52, 179.55, 153.54, 142.61, 136.12, 135.47, 132.69, 131.04, 130.09, 128.60, 128.16, 128.13, 127.22, 125.98, 110.43, 109.30, 104.72, 37.50. HRMS: found *m/z* 357.0556; calculated for C₂₀H₁₄O₃S,

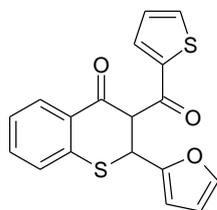
[M+Na]⁺ 357.0556.

3-Benzoyl-2-(5-methylfuran-2-yl)thiochroman-4-one (4b). Yield 0.47 g (68%). M.p.

202–204 °C. ¹H NMR (300 MHz, CDCl₃) δ 17.21 (s, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.19 (m, 8H), 5.92 (d, *J* = 2.6 Hz, 1H), 5.75 (d, *J* = 1.8 Hz,



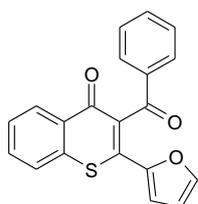
1H), 5.07 (s, 1H), 2.22 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 190.59, 179.39, 152.38, 151.38, 136.24, 135.65, 132.57, 130.97, 130.12, 128.54, 128.19, 128.06, 127.28, 125.84, 110.40, 106.46, 104.76, 37.60, 13.63. HRMS: found *m/z* 371.0712; calculated for C₂₁H₁₆O₃S, [M+Na]⁺ 371.0704.



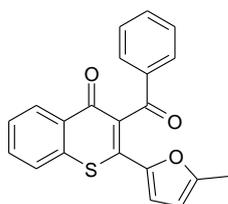
2-(2-Furyl)-3-(thiophen-2-ylcarbonyl)thiochroman-4-one (4c). Yield 67%. M.p. 142–144 °C. ¹H NMR (300 MHz, CDCl₃) δ 17.61 (s, *J* = 26.7 Hz, 1H), 8.30 – 7.94 (m, 1H), 7.70 (ddd, *J* = 15.9, 5.0, 3.0 Hz, 2H), 7.56 – 6.98 (m, 4H), 6.38 – 5.96 (m, 3H), 5.51 (d, *J* = 22.2 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 182.31, 178.83, 153.03, 142.92, 139.82, 134.73, 132.57, 132.31, 131.22, 130.11, 128.17, 128.02, 127.92, 126.10, 110.67, 109.66, 104.08, 37.43.

HRMS: found *m/z* 363.0120; calculated for C₁₈H₁₂O₃S₂ [M+Na]⁺ 363.0115

Preparation of thiochromones 1a–c (general procedure). Mixture of two forms **4a–c** / **4'a–c** (1 mmol) was dissolved in dioxane (2 ml), then SeO₂ was added (1.5 mmol) and the mixture was refluxed until TLC showed disappearance of the starting material. Dioxane was evaporated under reduced pressure, the residue was dissolved in chloroform (5 ml) and filtered through a small column filled with silica gel and eluted using the mixture of CH₂Cl₂–petroleum ether (1:1). After evaporation of the eluent, yellow crystals were washed with ethanol.



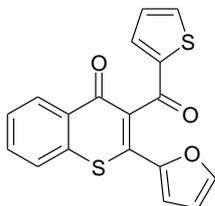
3-Benzoyl-2-(2-furyl)thiochromone (1a). Yield 0.3 g (90%) M.p. 235–237 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.48 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 7.4 Hz, 2H), 7.68 (d, *J* = 3.7 Hz, 2H), 7.62 – 7.51 (m, 2H), 7.50 – 7.39 (m, 3H), 6.86 (d, *J* = 3.6 Hz, 1H), 6.45 (dd, *J* = 3.6, 1.7 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 195.46, 179.16, 146.87, 145.74, 138.36, 136.54, 136.20, 133.59, 132.11, 130.78, 130.42, 129.05, 128.84, 128.75, 127.97, 126.20, 114.90, 112.77. HRMS: calculated for C₂₀H₁₂O₃S, [M+H]⁺ 333.0580; found *m/z* 333.0585; calculated for C₂₀H₁₂O₃S [M+Na]⁺ 355.0399; found *m/z* 355.0401; calculated for C₂₀H₁₂O₃S [M+K]⁺ 371.0139; found *m/z* 371.0139.



3-Benzoyl-2-(5-methylfuran-2-yl)thiochromone (1b). Yield 0.32 g (92%). M.p. 192–194 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.46 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 7.3 Hz, 2H), 7.64 (d, *J* = 3.9 Hz, 2H), 7.59 – 7.49 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 6.75 (d, *J* = 3.5 Hz, 1H), 6.04 (d, *J* = 3.3 Hz, 1H), 2.17 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 195.76, 179.17, 156.78, 145.10, 138.36, 136.70, 136.15, 133.44, 132.00, 130.41, 129.42, 129.03, 128.72, 128.68, 127.80, 126.15, 116.40, 109.46, 13.55. HRMS: calculated for C₂₁H₁₄O₃S [M+H]⁺ 347.0736; found *m/z*

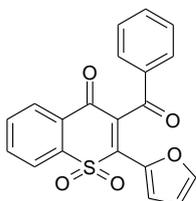
347.0737; calculated for $C_{21}H_{14}O_3S$ $[M+Na]^+$ 369.0556; found m/z 369.0557; calculated for $C_{21}H_{14}O_3S$ $[M+K]^+$ 385.0295; found m/z 385.0295.

2-(2-Furyl)-3-(thiophen-2-ylcarbonyl)thiochromone (1c). Yield 78%. M.p. 227–229 °C. 1H NMR (300 MHz, $CDCl_3$) δ 8.50 (d, $J = 8.0$ Hz, 1H), 7.74 – 7.50 (m, 6H), 7.05 (t, $J = 4.3$ Hz, 1H), 6.92 (d, $J = 3.6$ Hz, 1H), 6.47 (dd, $J = 3.3, 1.5$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.31, 178.77, 146.69, 145.87, 143.87, 138.91, 136.07, 134.74, 134.02, 132.17, 130.47, 130.42, 128.89, 128.25, 128.04, 126.24, 115.16, 112.90. HRMS: found m/z 339.0144; calculated for $C_{18}H_{10}O_3S_2$, $[M+H]^+$ 339.0147; found m/z 360.9964; calculated for $C_{18}H_{10}O_3S_2$ $[M+Na]^+$ 360.9959; found m/z 376.9703; calculated for $C_{18}H_{10}O_3S_2$ $[M+K]^+$ 376.9703.

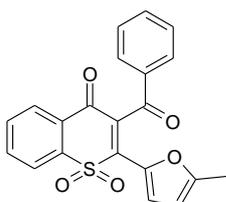


Preparation of 3-benzoyl-2-(2-furyl)-1,1-dioxidothiochromones 5a–c (general procedure). Thiochromone **1a,b** (0.15 mmol) was dissolved in CH_2Cl_2 (5 ml) and *m*-CPBA (0.35 mmol) at 0 °C was added. The solution was stirred for 2 h at 0 °C, then it was stirred at r.t. until TLC showed disappearance of the starting material (*ca.* 2 days). The solution was washed with sodium hydrogen carbonate solution, washed with water and dried under anhydrous Na_2SO_4 , the solvent was evaporated giving bright yellow solid.

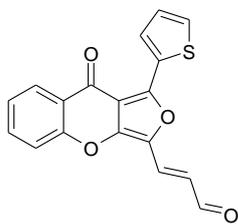
3-Benzoyl-2-(2-furyl)-1,1-dioxidothiochromone (5a). Yield 35 mg (65%). M.p. 223–225 °C. 1H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, $J = 7.8$ Hz, 1H), 8.18 (s, $J = 7.9$ Hz, 1H), 8.01 – 7.89 (m, 3H), 7.82 (t, $J = 7.7$ Hz, 1H), 7.64 (d, $J = 3.6$ Hz, 1H), 7.60 (d, $J = 7.4$ Hz, 1H), 7.54 – 7.42 (m, 3H), 6.60 (d, $J = 2.3$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.04, 177.43, 148.21, 141.20, 140.69, 139.37, 135.96, 134.84, 134.10, 133.40, 131.40, 128.95, 128.87, 128.61, 128.44, 123.32, 121.51, 113.68. HRMS: calculated for $C_{20}H_{12}O_5S$, $[M+H]^+$ 365.0478; found m/z 365.0474; calculated for $C_{20}H_{12}O_5S$ $[M+Na]^+$ 387.0298; found m/z 387.0290; calculated for $C_{20}H_{12}O_5S$ $[M+K]^+$ 403.0037; found m/z 403.0037.



3-Benzoyl-2-(5-methylfuran-2-yl)-1,1-dioxidothiochromone (5b). Yield 32 mg (57%). M.p. 212–214 °C. 1H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, $J = 7.5$ Hz, 1H), 8.16 (d, $J = 7.5$ Hz, 1H), 8.06 – 7.74 (m, 4H), 7.71 – 7.38 (m, 4H), 6.23 (s, 1H), 2.05 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.42, 177.40, 160.13, 140.68, 139.76, 139.14, 136.26, 134.59, 133.83, 133.31, 129.61, 128.84, 128.82, 128.36, 123.52, 123.20, 110.86, 13.61. HRMS: found m/z 379.0632; calculated for $C_{21}H_{14}O_5S$ $[M+H]^+$ 379.0635; found m/z 401.0454; calculated for $C_{21}H_{14}O_5S$ $[M+Na]^+$ 401.0454; found m/z 417.0212; calculated for $C_{21}H_{14}O_5S$ $[M+K]^+$ 417.0194.

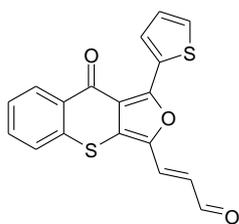


Photorearrangement of 2-(2-furyl)-3-(thiophene-2-carbonyl)chromone (1d) into 3-(9-oxo-1-(2-thienyl)-9H-2,4-dioxacyclopenta[b]naphthalen-3-yl)propenal.

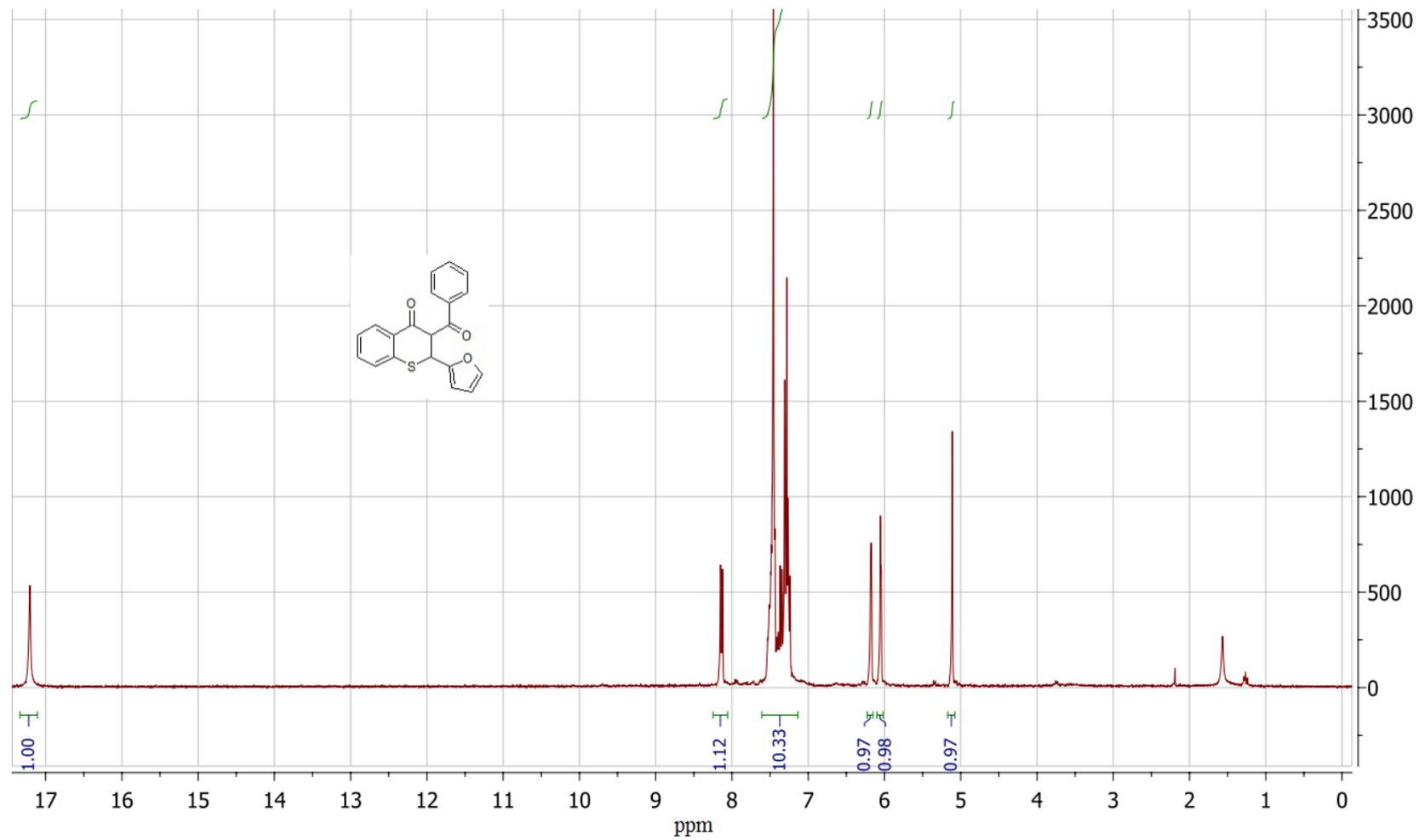


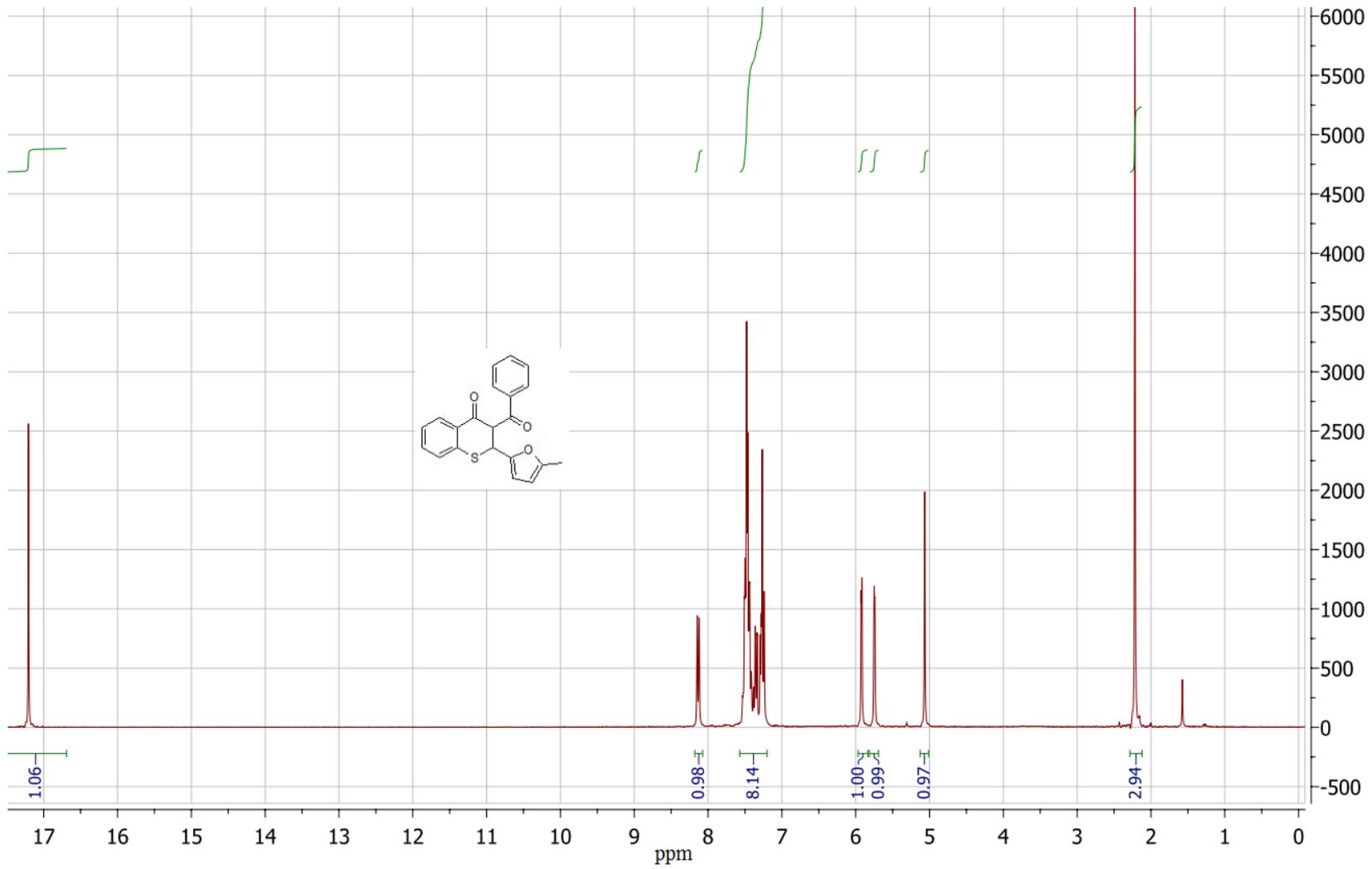
2-(2-Furyl)-3-(thiophen-2-ylcarbonyl)chromone (**1d**) (0.3 g, 0.93 mmol) was dissolved in dichloromethane (1 l) and placed into photoreactor (Ace photochemical reaction assembly capacity 1000 ml, AC input 230 V, Aceglass) equipped with an UV lamp with a capacity of 450 W, using light filter made of Pyrex glass. The solution was irradiated for 1.5 h (TLC-control), the solvent was evaporated under reduced pressure. The product was purified by column chromatography (petroleum ether–ethyl acetate 20:1). Yield 0.03 g (10%). M.p. 194–196 °C (decomp.). ¹H NMR (600 MHz, CDCl₃) δ 9.67 (d, *J* = 7.9 Hz, 1H), 8.70 (d, *J* = 3.7 Hz, 1H), 8.28 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.64 (d, *J* = 4.8 Hz, 1H), 7.47 (d, *J* = 15.6 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.22 (m, 1H), 6.68 (dd, *J* = 15.6, 7.9 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 192.28, 173.59, 156.27, 151.83, 147.66, 135.55, 132.77, 132.16, 131.95, 131.54, 130.94, 128.75, 127.21, 124.67, 123.68, 122.11, 117.73, 110.45. HRMS: found *m/z* 323.0373; calculated for C₁₈H₁₀O₄S [M+H]⁺ 323.0375; found *m/z* 345.0192; calculated for C₁₈H₁₀O₄S [M+Na]⁺ 345.0190. ESI-MS (70 eV), *m/z* (I, %): 322 (100), 294 [M – CHO]⁺ (12), 268 [M – CHCHCHO]⁺ (71), 239 [M – CHCHCO – CO]⁺ (26).

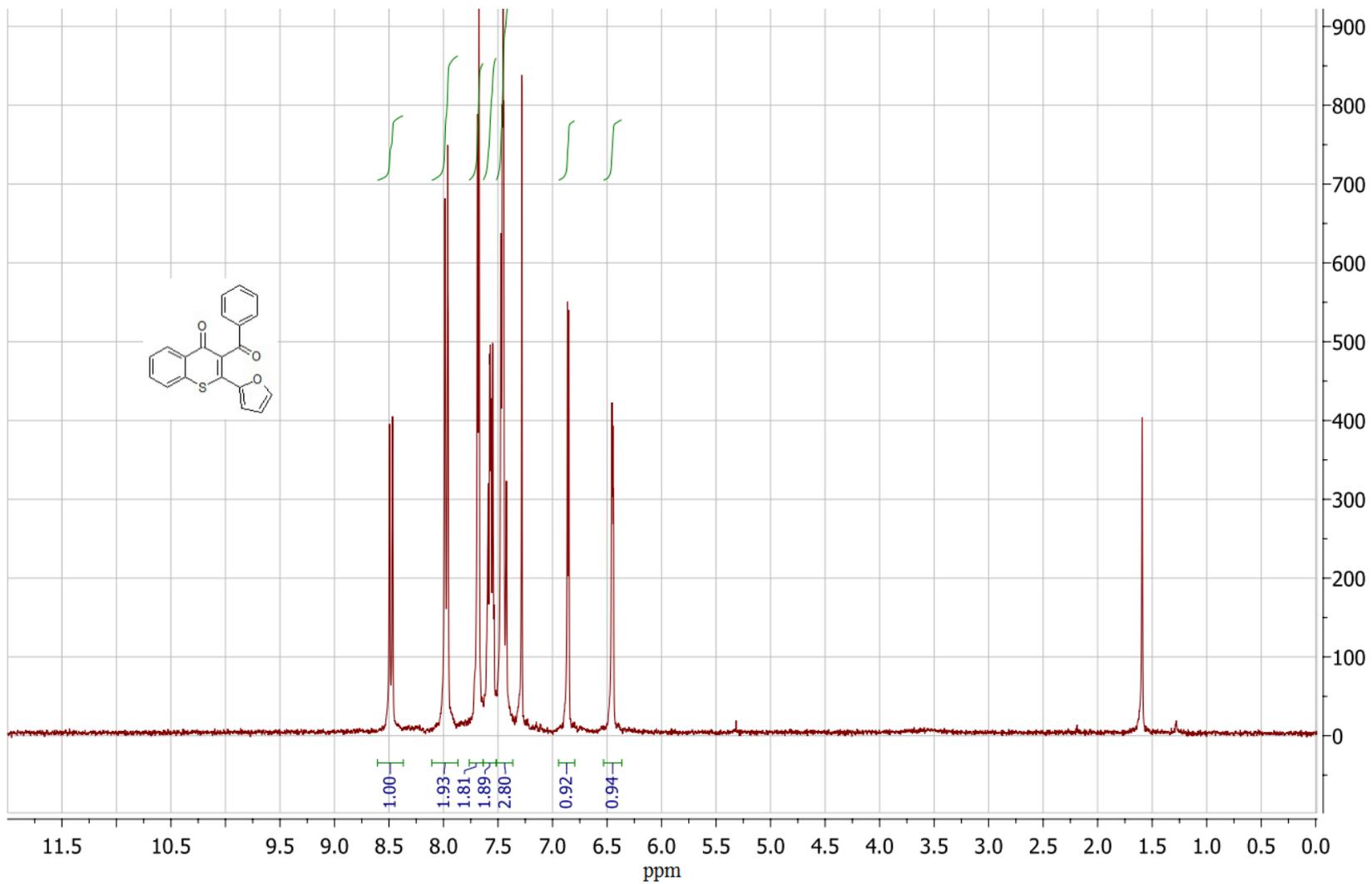
Photorearrangement of 2-(2-furyl)-3-(thiophen-2-ylcarbonyl)thiochromone (1c).

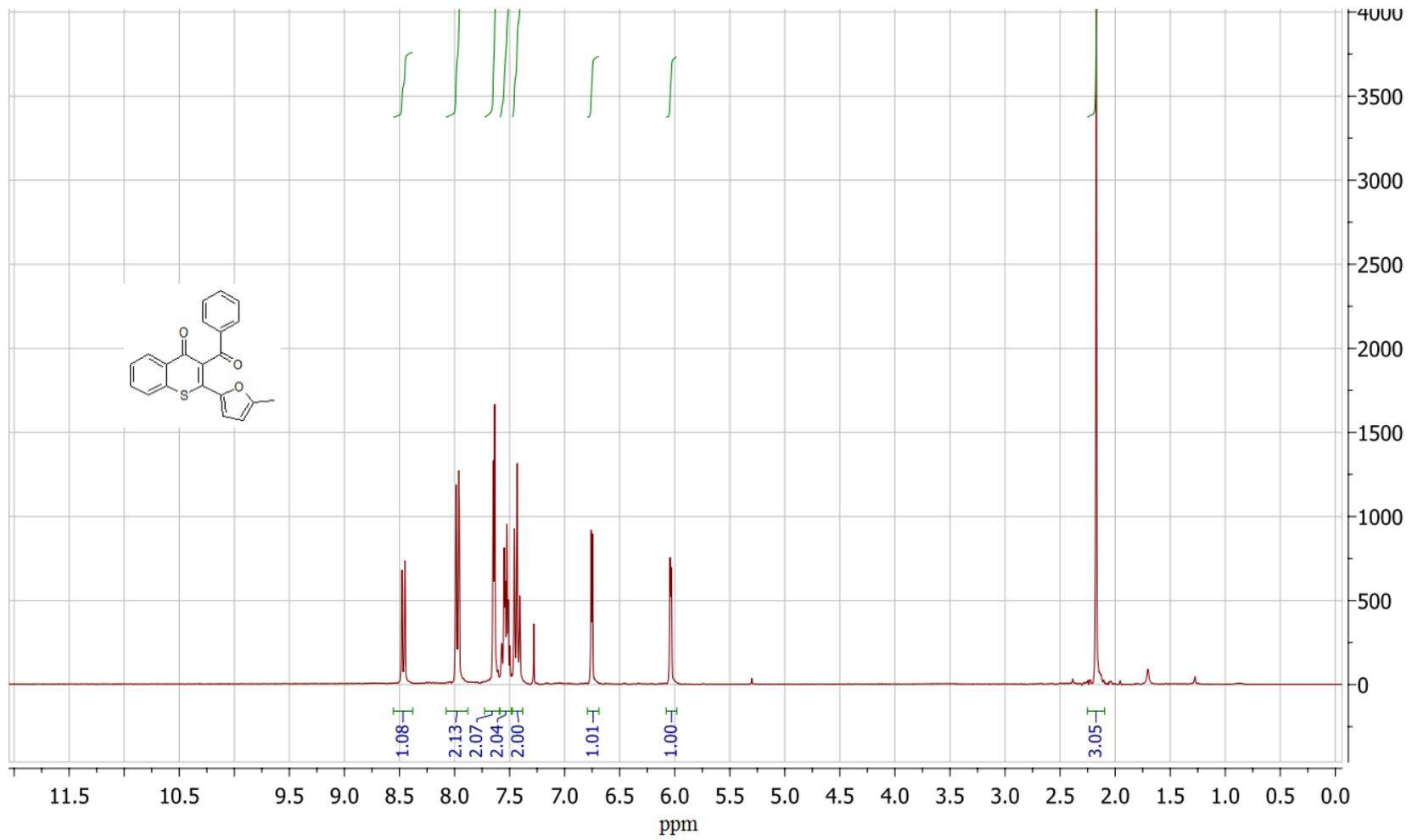


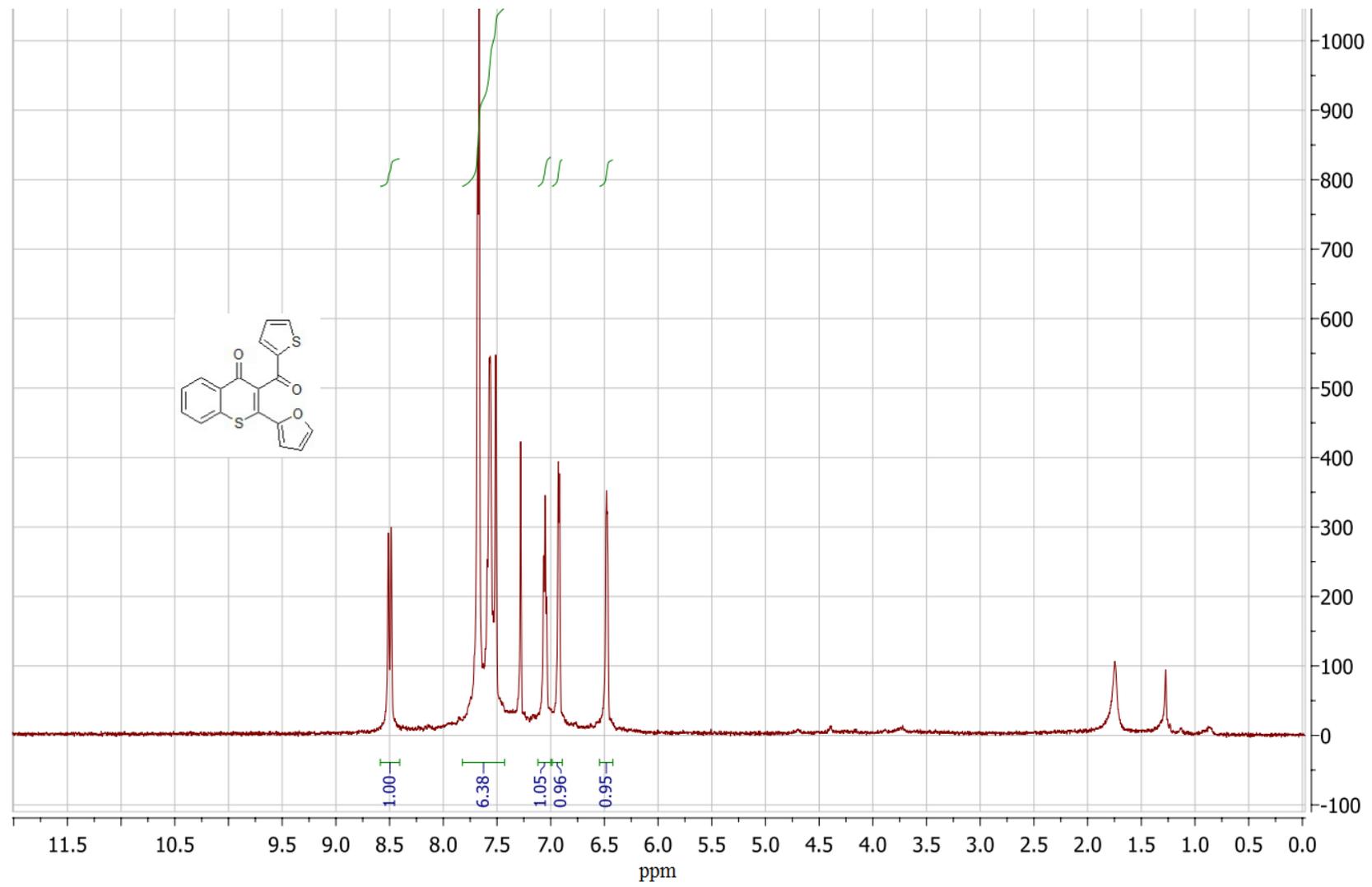
2-(2-Furyl)-3-(thiophen-2-ylcarbonyl)thiochromone (**1c**) (70 mg, 0.2 mmol) was dissolved in acetonitrile (15 ml) and degassed. The solution was irradiated with UV light using 4 W UV lamp at wavelength of 365 nm for 5 h. The residue was subjected to column chromatography. After 8 experiments total yield of the photoproduct was 2 mg. ¹H NMR spectrum of the solution showed the following signals along with the signals of the starting material: doublet at 9.72 (d, *J* 7.9 Hz) of an aldehyde group; signal at 6.65 – 6.75 (dd, *J* 15.6, 7.9 Hz) of the proton at the α -position towards an aldehyde group. ESI-MS (70 eV), *m/z* (I, %): 332 (100), 303 [M – CHO]⁺ (26), 278 [M – CHCHCO]⁺ (16), 250 [M – CHCHCO – CO]⁺ (13).

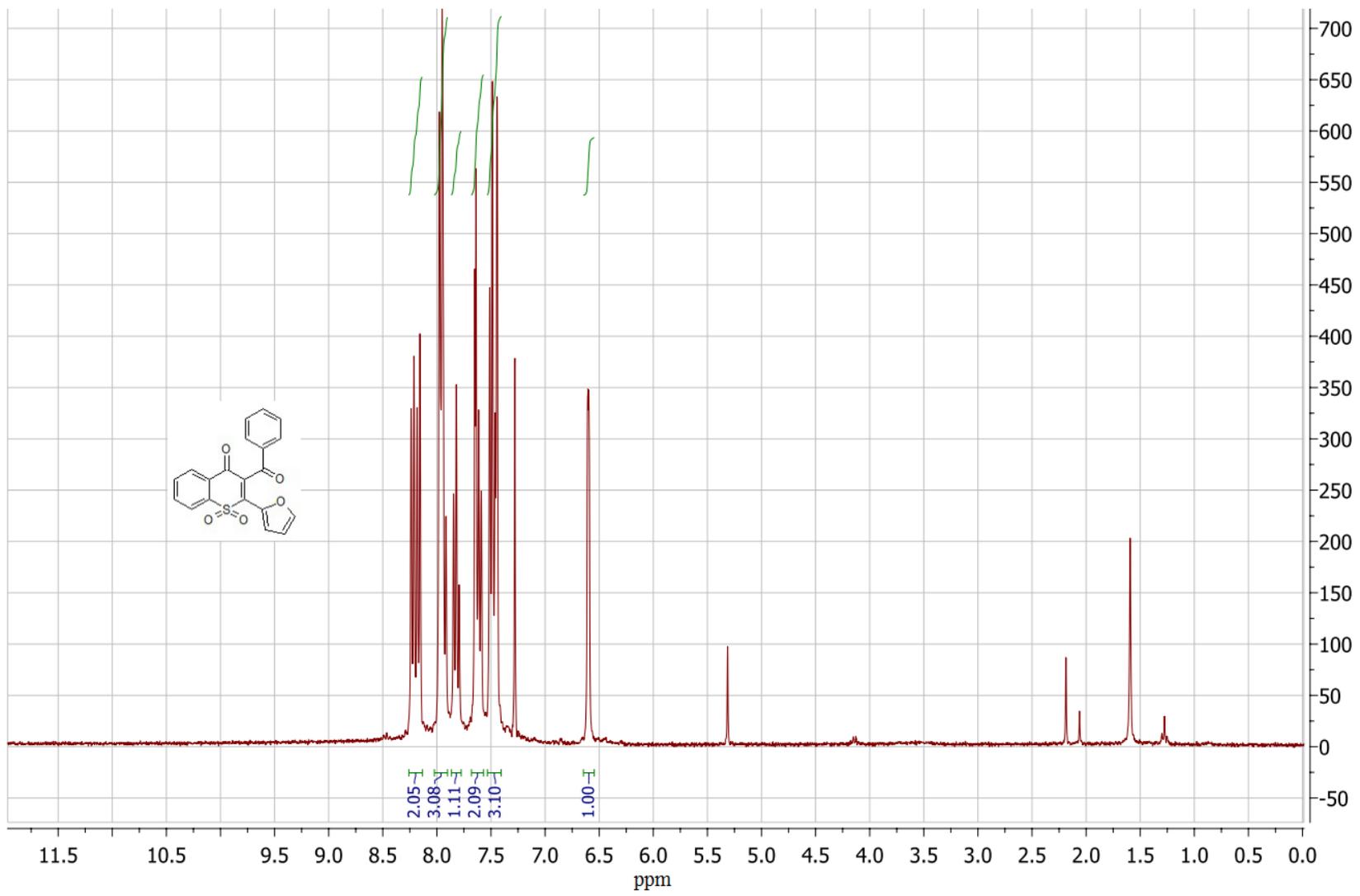


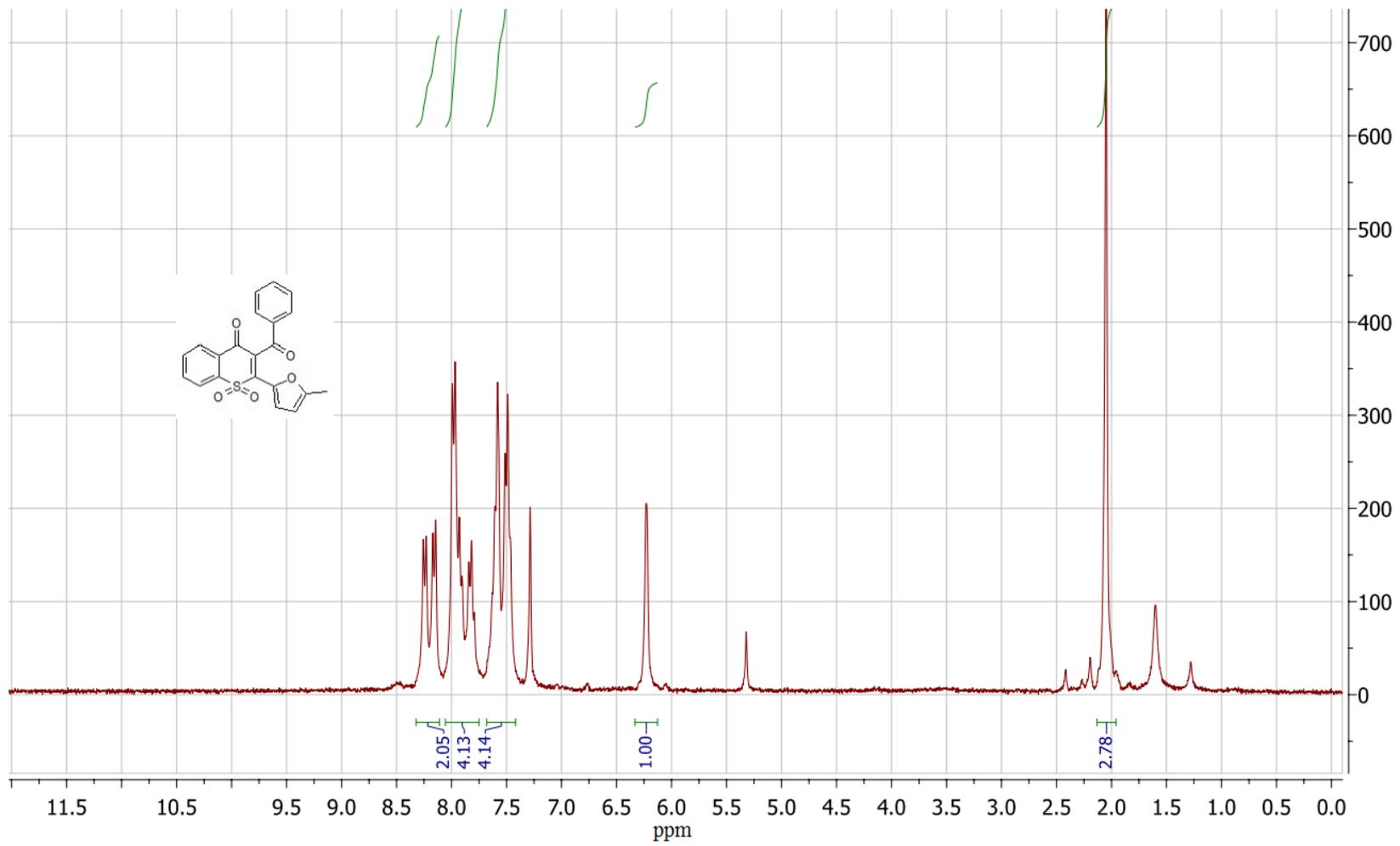


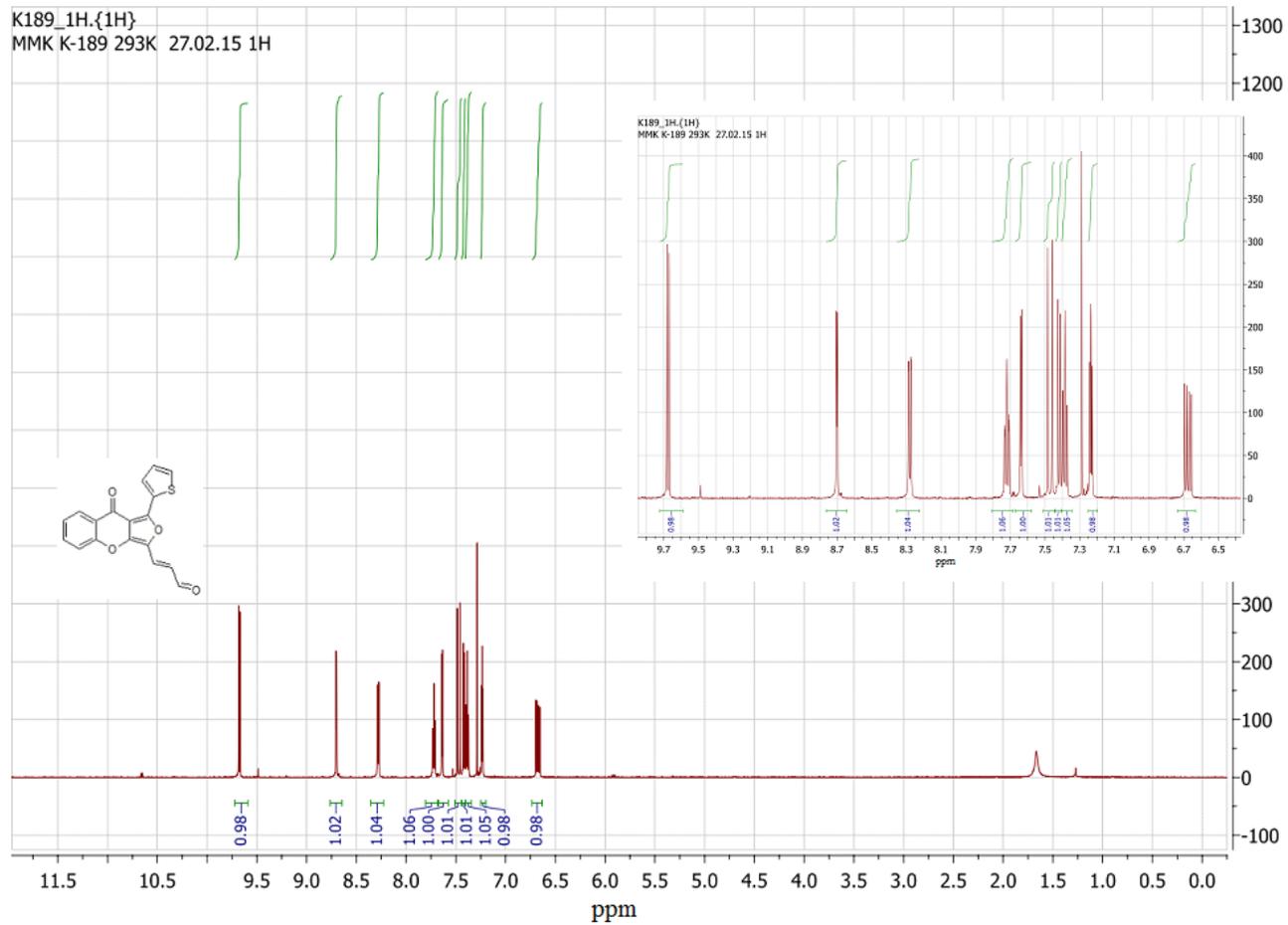


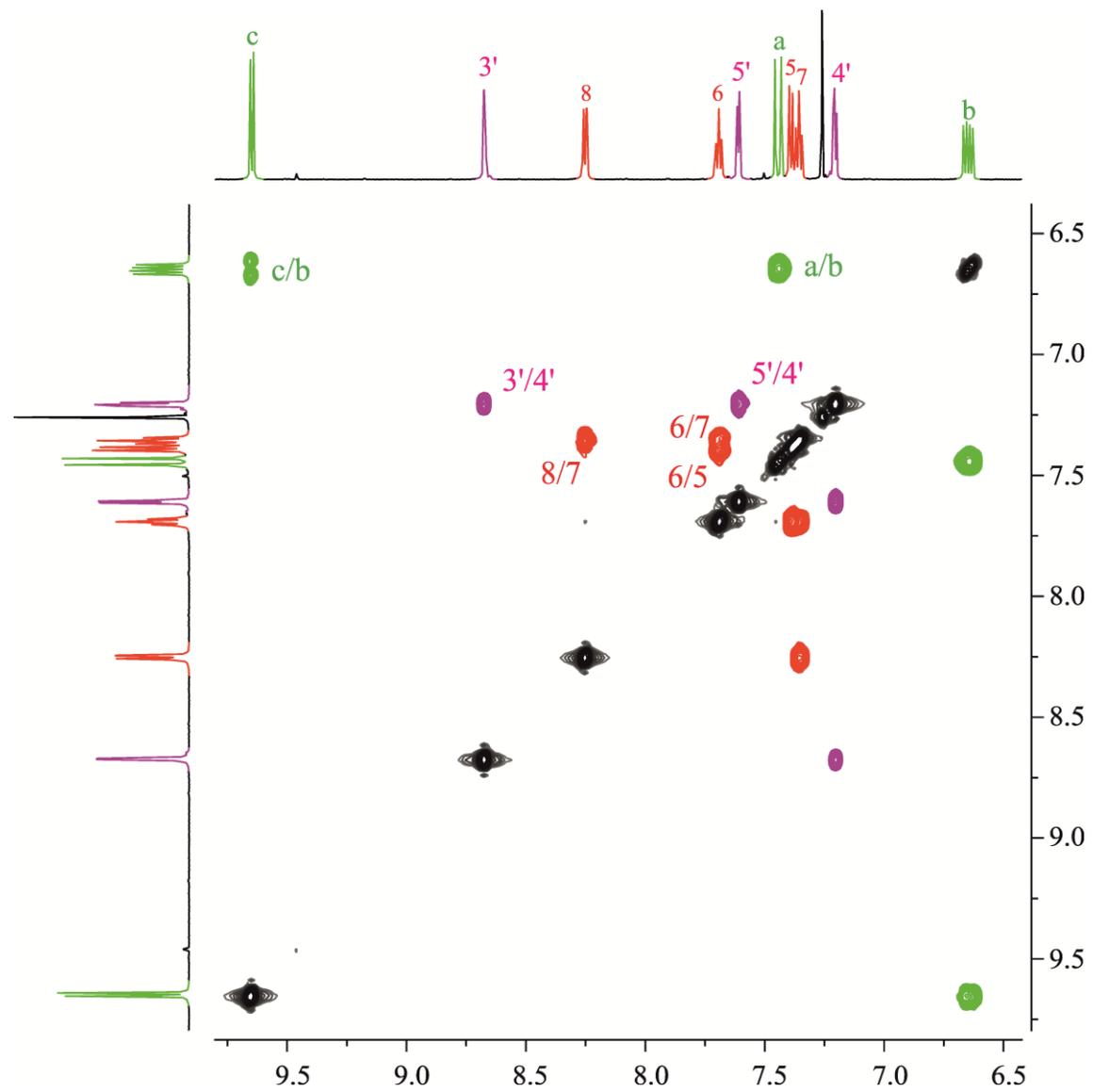




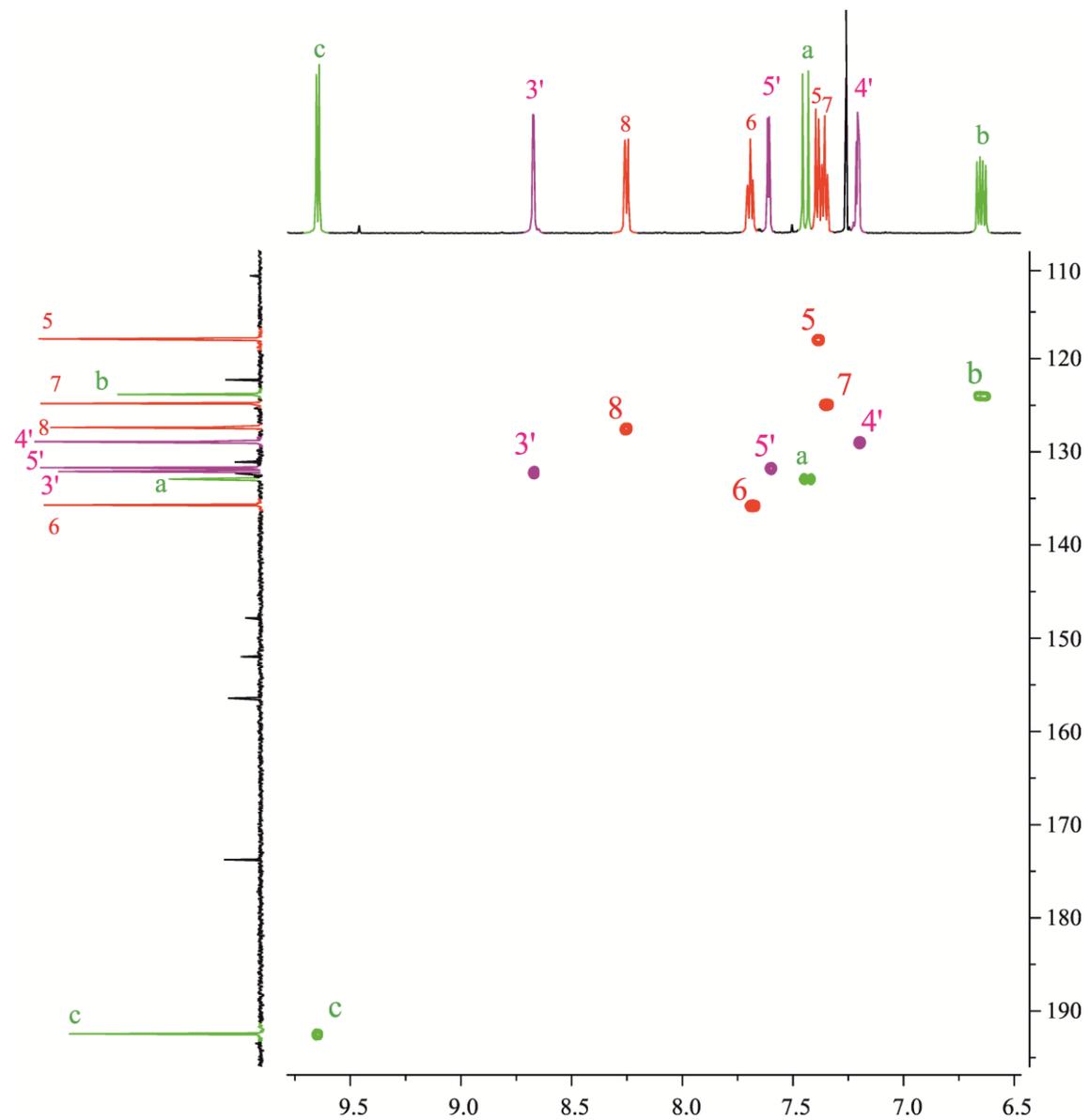




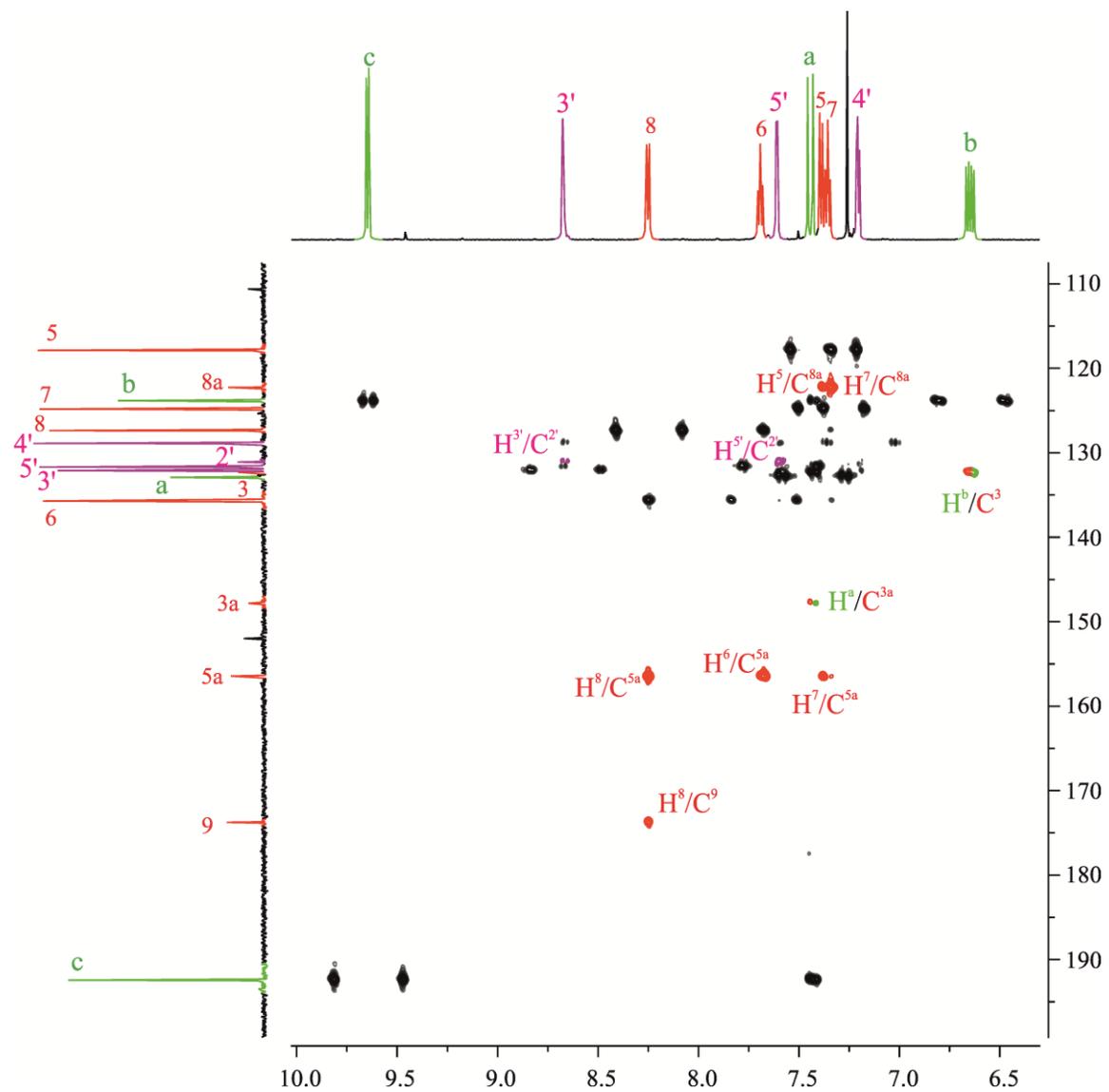




Fragment of COSY-spectrum of (3-(9-oxo-1-thiophen-2-yl-9H-2,4-dioxacyclopenta[b]naphthalen-3-yl)-propenal).



Fragment of HSQC-spectrum of (3-(9-oxo-1-thiophen-2-yl-9H-2,4-dioxacyclopenta[b]naphthalen-3-yl)-propenal).



Fragment of HMBC-spectrum of (3-(9-oxo-1-thiophen-2-yl-9H-2,4-dioxacyclopenta[b]naphthalen-3-yl)-propenal).

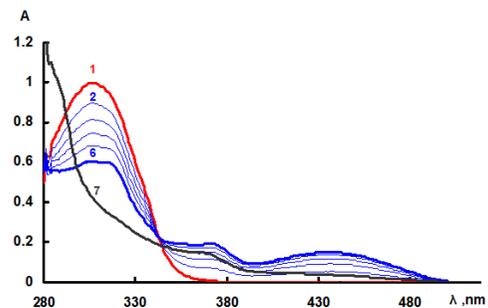


Figure S1 Absorption spectra of compound **1d** in toluene before (1), after successive UV irradiation through the light filter UFS-1 (2-6) and after photodegradation under unfiltered irradiation (7).

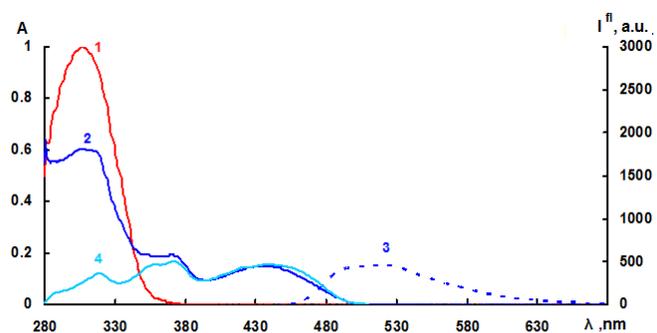


Figure S2 Spectra of absorption (1,2), fluorescence under excitation irradiation 435 nm (3) and fluorescence excitation measured at 520 nm (4) of compound **1d** in toluene before (1) and after UV irradiation through a light filter UFS-1 (2,3,4).

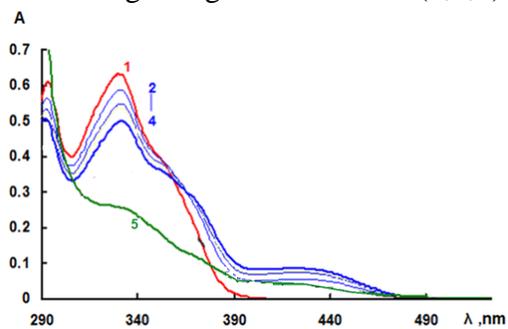


Figure S3 Absorption spectra of compound **1a** in toluene before (1), after successive UV irradiation through the light filter UFS-1 (2-4), and after photodegradation under unfiltered irradiation (5).

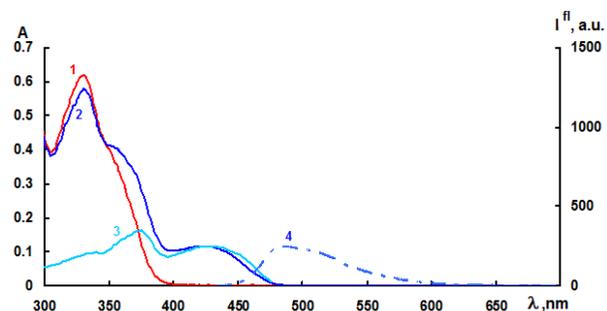


Figure S4 Spectra of absorption (1,2), fluorescence excitation measured at 486 nm (4) and fluorescence under excitation irradiation 424 nm (3) of compound **1a** in toluene before (1) and after UV irradiation through a light filter UFS-1 (2,3,4).

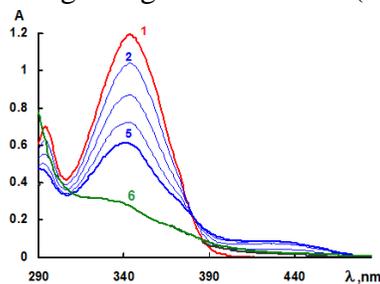


Figure S5 Absorption spectra of compound **1b** in toluene before (1), after successive UV irradiation through the light filter UFS-1 (2-5), and after photodegradation under unfiltered irradiation (6).

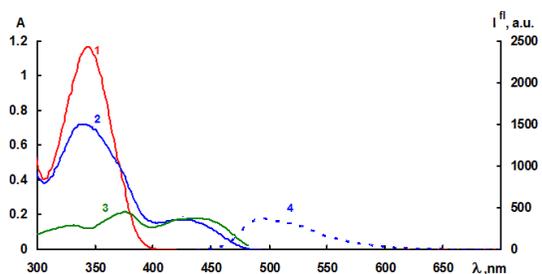


Figure S6 Spectra of absorption (1,2), and fluorescence under excitation irradiation 422 nm (3), fluorescence excitation measured at 491 nm (4) of compound **1b** in toluene before (1) and after UV irradiation through a light filter UFS-1 (2,3,4).

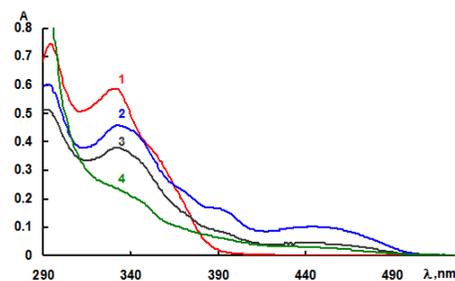


Figure S7 Absorption spectra of compound **1c** in toluene before (1), after successive UV irradiation through the light filter UFS-1 (2), visible irradiation through the light filter ZhS-10 (3), and after photodegradation under unfiltered irradiation (4).

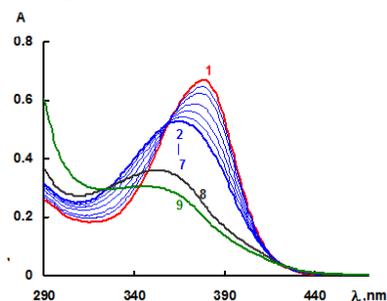


Figure S8 Absorption spectra of compound **5a** in toluene before (1), after successive UV irradiation through the light filter UFS-1 (2-7), after photodegradation under UV irradiation through the light filter UFS-1 (8), and following unfiltered irradiation (9).

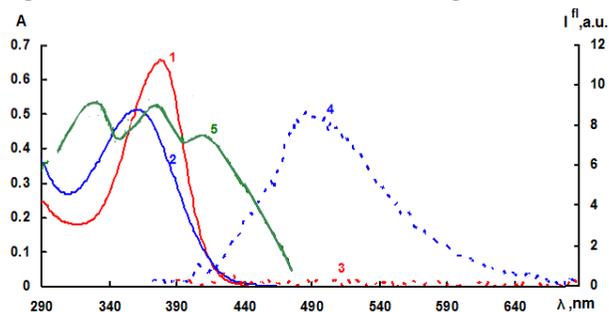


Figure S9 Spectra of absorption (1,2), fluorescence under excitation irradiation 379 nm (3) and 362 nm (4), fluorescence excitation measured at 488 nm (4) of compound **5a** in toluene before (1,3) and after UV irradiation through a light filter UFS-1 (2,4,5).

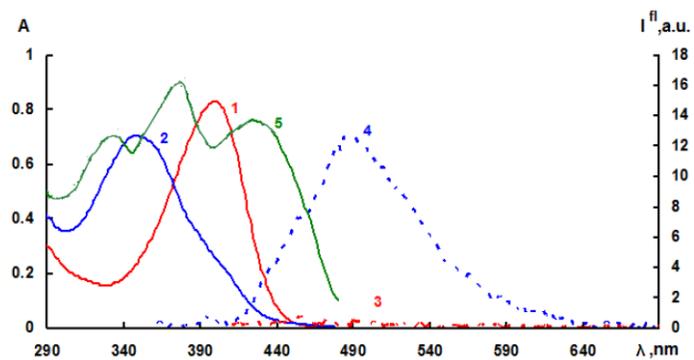


Figure S10 Spectra of absorption (1,2), fluorescence under excitation irradiation 400 nm (3) and 342 nm (4), fluorescence excitation measured at 490 nm (4) of compound **5b** in toluene before (1,3) and after UV irradiation through a light filter UFS-1 (2,4,5).