Electronic Supplementary Information for

Novel water-soluble multicolor halo- and photochromic switching system based on the nitrile-rich acceptor

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1. Experimental

1.1. Synthetic procedures

Synthesis of 2-([phenylimino]methyl)phenol 2.

Compound **2** was prepared according to the literature procedure [1].

Salicylaldehyde (5.02 g, 41.10 mmol) and aniline (5.84 g, 41.20 mmol) were stirred in 50 ml methanol for 100 minutes. Distilled water was then added dropwise, with stirring, to the yellow solution until the solution remained cloudy for a few seconds before turning translucent again. The mixture was cooled in an ice-bath and the resultant yellow crystalline product was filtered and washed with of cold water (10 ml) and methanol (10 ml) and then dried in a vacuum drying cabinet (1 Torr) over $CaCl_2$ for 2 days. Yield 7.17 g (89%).

Synthesis of sodium 3-formyl-4-hydroxybenzenesulfonate 4.

Compound **4** was prepared according to the literature procedure [1].

Concentrated sulfuric acid (10 ml of 98% H_2SO_4) was placed in a round-bottomed flask fitted with reflux condenser and 3.50 g (17.70 mmol) 2-([phenylimino]methyl)phenol **2** was added slowly with stirring. The mixture was heated at 100–105 °C for 2.5 hours. The hot solution was poured carefully into a beaker containing 100 ml of ice water. A yellow product precipitated immediately. The suspension was then reheated until all the product had dissolved to form a bright orange solution. Undissolved particles were filtered by gravity from the hot solution and the filtrate left to stand at room temperature. The yellow-brown product **3** was filtered and washed with small portions of cold water. The resulted crude product **3** without an additional treatment* was mixed with Na_2CO_3 (1.03 g, 9.80 mmol) and boiled vigorously in an open flask containing 15 ml distilled water for 3 hours. The water was replenished as necessary. Glacial acetic acid (10 ml) was then added to the cooled solution. The same amount of ethanol was added, and the solution cooled in an ice-bath for several hours. The fine beige crystals of compound **4** were filtered and washed with cold ethanol and dried in vacuum drying cabinet (1 Torr) over $CaCl_2$ for 3 days. Yield 1.35 g (34%).

Synthesis of 2-(3-cyano-4,5,5-trimethylfuran-2(5*H*)-ylidene)malononitrile TCF.

Compound TCF was prepared according to the literature procedure [4].

A mixture of 92% 3-hydroxy-3-methylbutan-2-one (9.5 g, 85.6 mmol), malononitrile (12.3 g, 186 mmol), two drops of glacial acetic acid and pyridine (50 ml) was stirred at room temperature for 24 hours. The reaction temperature was controlled without exceeding the room temperature by the use of an ice bath at the beginning of the reaction. The reaction mixture was then poured into 800 ml ice water with vigorous stirring. The precipitate was collected by vacuum filtration and recrystallized from ethanol to give 8.84 g (52% yield) of white crystals.

*The use of a crude product **3** is the most efficient approach for the rationalized synthesis of the desired aldehyde **4** [1-3].

1.2. Spectral data

Characterization of compound **2**. Mp 50-52 °C (lit. [5] 50-51 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.02-6.95 (2H, m, Ar), 7.29-7.35 (1H, m, Ar), 7.38-7.50 (5H, m, Ar), 7.64-7.69 (1H, m, Ar), 8.96 (1H, s, CHN), 13.11 (1H, s, OH). ^{13}C NMR (125.76 MHz, DMSO-d_6): δ 116.56, 119.09, 119.27, 121.32, 126.89, 129.41, 132.54, 133.23, 148.07, 160.27, 163.48. MS, (EI, 70 eV): *m/z* (%) 197 (100), 196 (59).

Characterization of compound **4**. Mp 330-332 °C (lit. [1] 331-334 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.96 (1H, d, *J*=8.5 Hz, C_6H_3), 7.74 (1H, dd, *J*=2.3, 8.5 Hz, C_6H_3), 7.92 (1H, d, *J*=2.3 Hz, C_6H_3), 10.27 (1H, s, COH), 10.92 (1H, s, OH). ^{13}C NMR (125.76 MHz, DMSO-d_6): δ 116.61, 121.09, 126.26, 133.72, 139.73, 160.87, 191.34. MS, (EI, 70 eV): *m/z* (%) 200 (67).

Characterization of compound **TCF**. Mp 201-203 °C (lit. [4] 203 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.60 (6H, s, $2CH_3$), 2.37 (3H, s, CH_3). ^{13}C NMR (125.76 MHz, DMSO-d_6): δ 14.88, 23.91, 55.50, 102.00, 104.33, 110.63, 112.16, 112.87, 177.93, 186.41. MS, (EI, 70 eV): *m/z* (%) 199 (51), 184 (100).

2. Absorption spectra

2.1. Absorption spectra of compound 1 in water at certain pH values

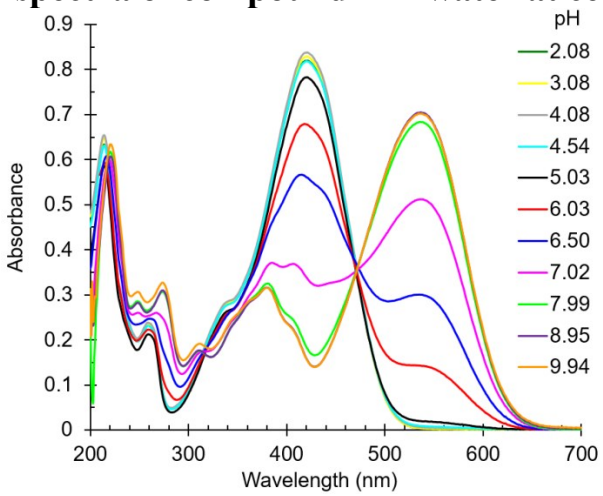

Fig. 1. UV-Vis spectra of compounds **1** in H_2O at different values pH ($C = 2.5 \times 10^{-5}$ M, phosphate buffer, 20°C)

2.2. Absorption spectra of compound 1 in in phosphate buffer before and after irradiation at certain pH values ($C = 2.5 \times 10^{-5}$ M, phosphate buffer, 20°C)

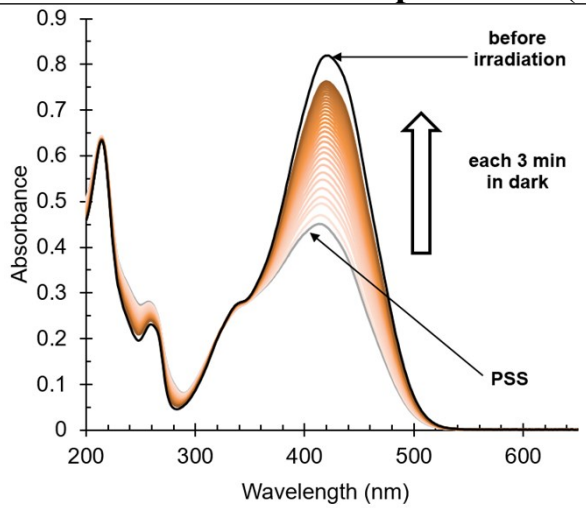

Fig. 2. Absorption spectra of compound **1** at pH 2.08

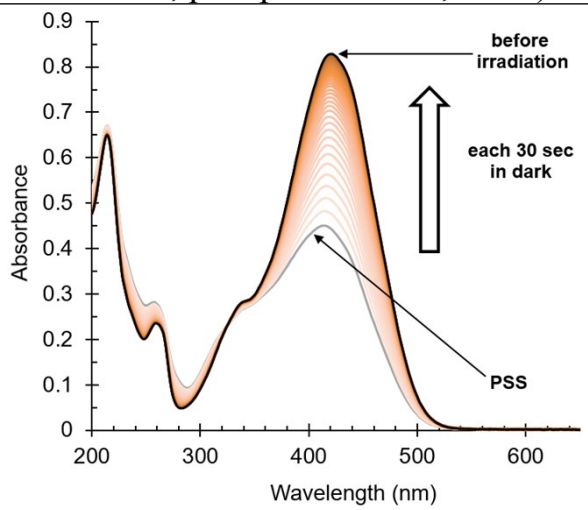

Fig. 3. Absorption spectra of compound **1** at pH 3.08

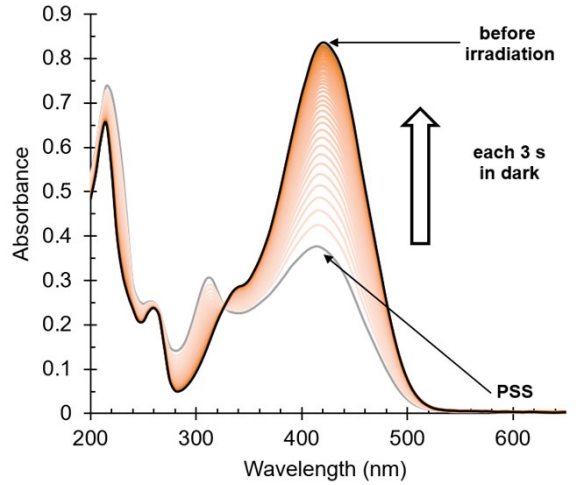

Fig. 4. Absorption spectra of compound 1 at pH 4.08

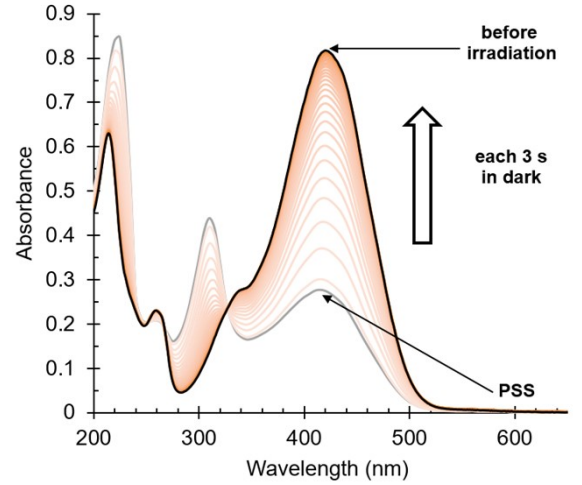

Fig. 5. Absorption spectra of compound 1 at pH 4.54

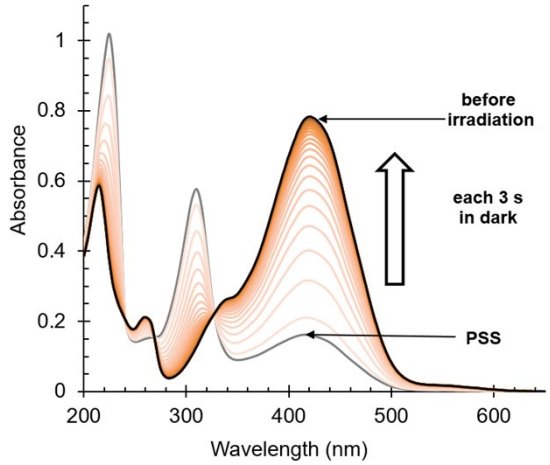

Fig. 6. Absorption spectra of compound 1 at pH 5.03

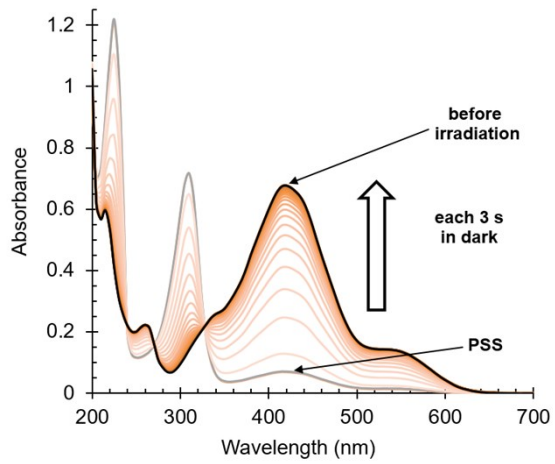

Fig. 7. Absorption spectra of compound 1 at pH 6.03

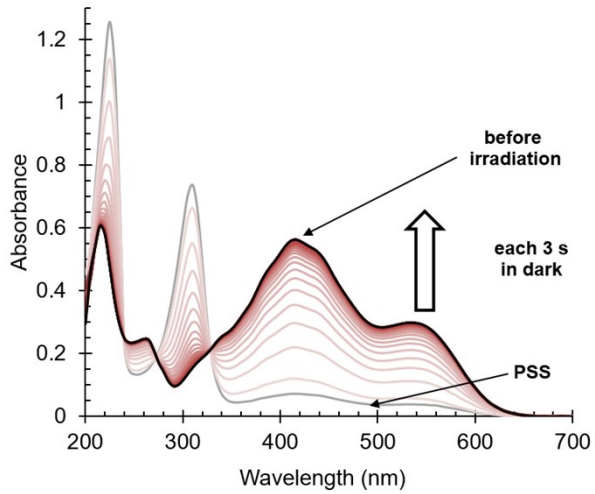

Fig. 8. Absorption spectra of compound 1 at pH 6.50

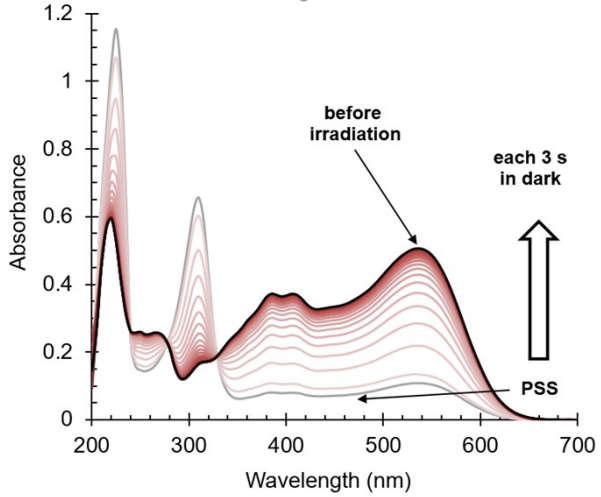

Fig. 9. Absorption spectra of compound 1 at pH 7.02

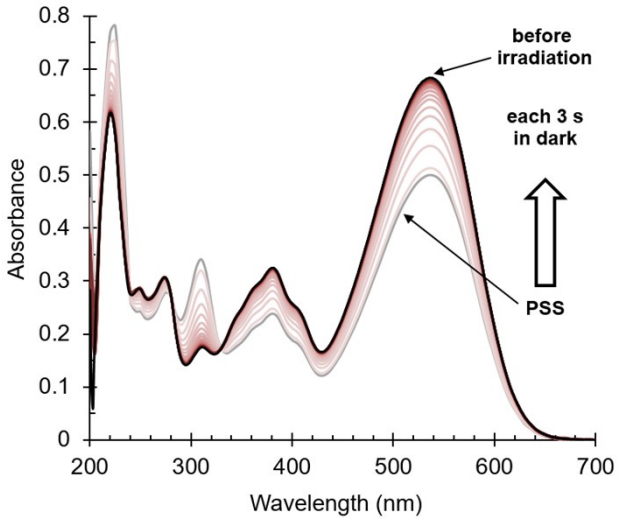

Fig. 10. Absorption spectra of compound 1 at pH 7.99

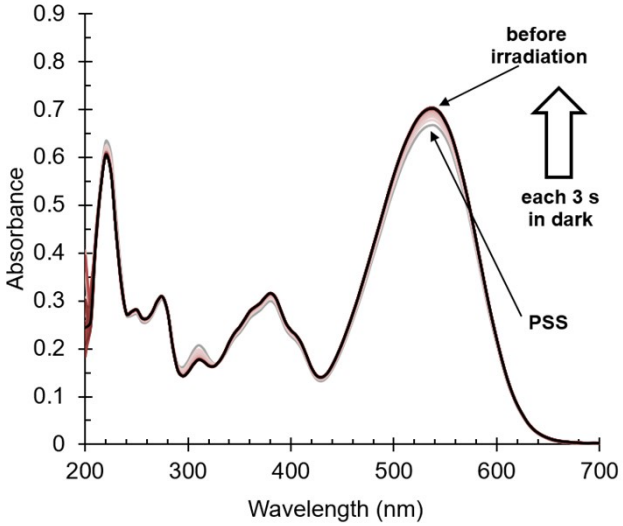

Fig. 11. Absorption spectra of compound 1 at pH 8.95

3. Determination of acidity constant pK_a^1 of compound 1 in water

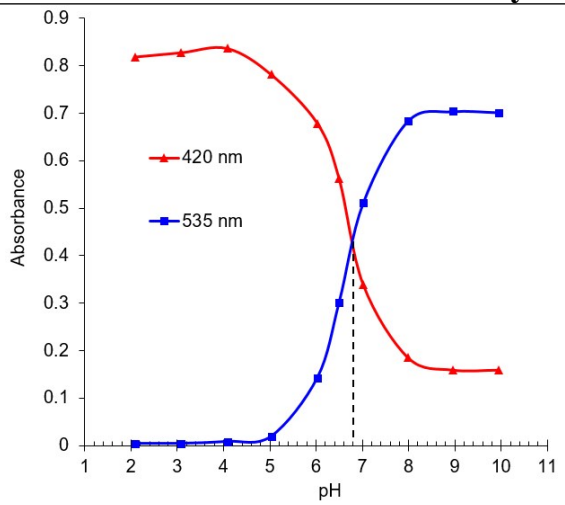

Fig. 12. Plot of absorbance at wavelengths of 420 nm and 535 nm vs. pH for the compound **1**

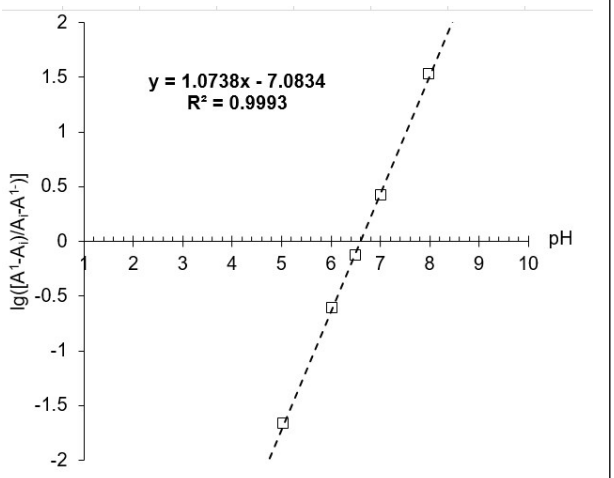

Fig. 13. linear regression of logarithmic absorbance ratio of **1** and **1**$^-$ forms vs. pH

4. Cyclicity of photochromic transformation of compound 1 at different values pH

($C = 2.5 \times 10^{-5}$ M, 20 °C)

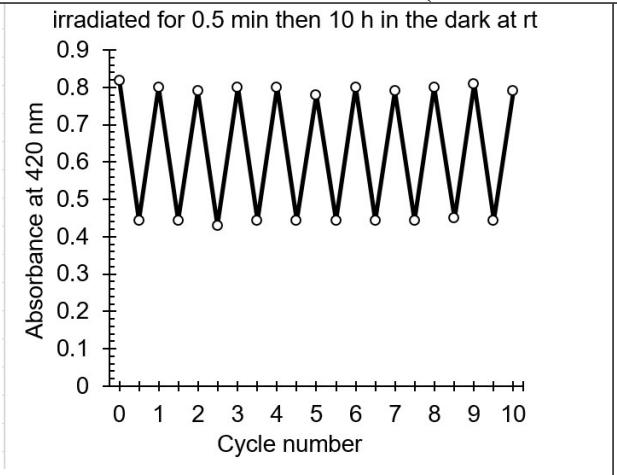

Fig. 14. Cyclicity of photochromic transformation of compound **1** at pH 2.08

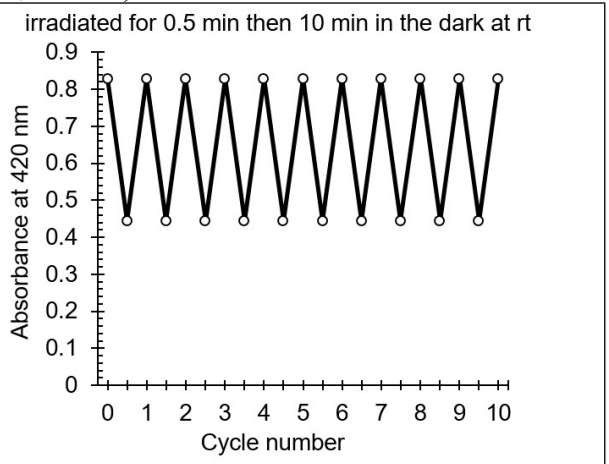

Fig. 15. Cyclicity of photochromic transformation of compound **1** at pH 3.08

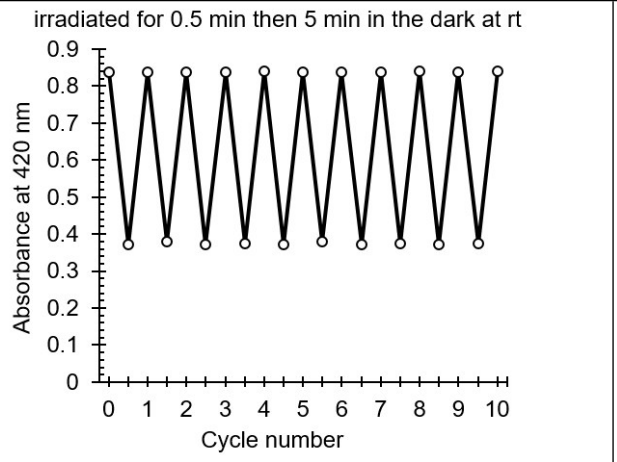

Fig. 16. Cyclicity of photochromic transformation of compound **1** at pH 4.08

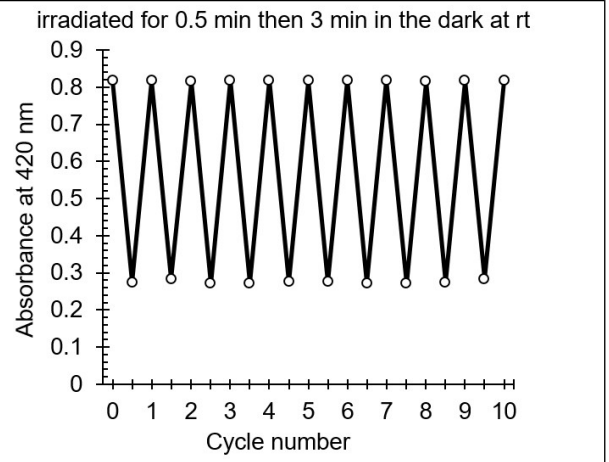

Fig. 17. Cyclicity of photochromic transformation of compound **1** at pH 4.54

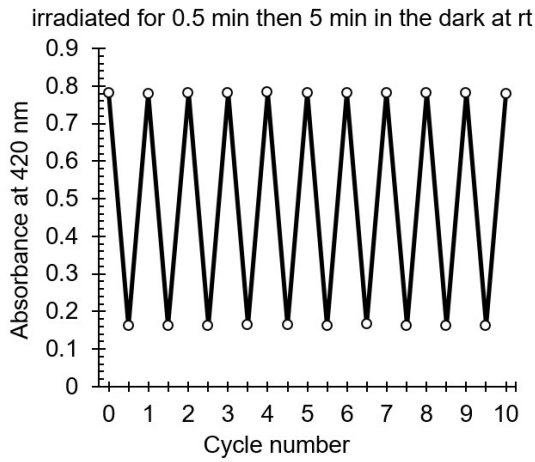

Fig. 18. Cyclicity of photochromic transformation of compound **1** at pH 5.03

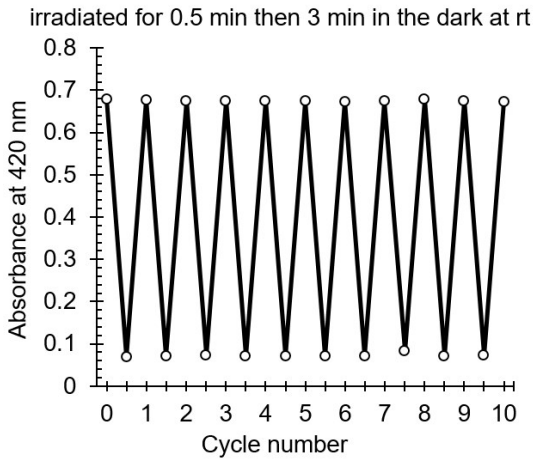

Fig. 19. Cyclicity of photochromic transformation of compound **1** at pH 6.03

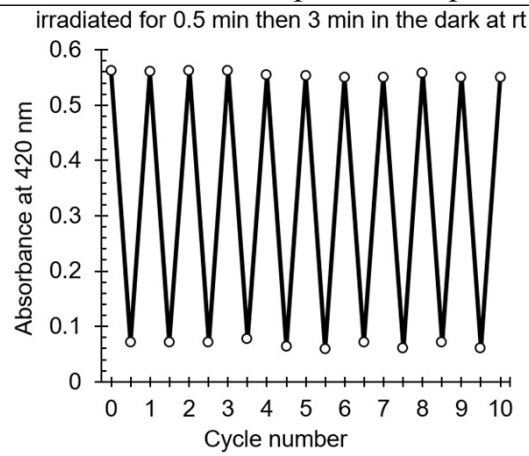

Fig. 20. Cyclicity of photochromic transformation of compound **1** at pH 6.50

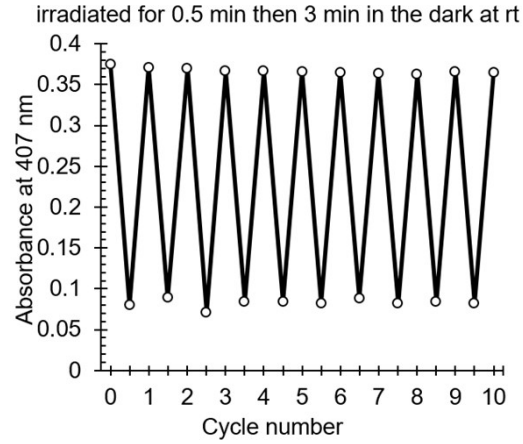

Fig. 21. Cyclicity of photochromic transformation of compound **1** at pH 7.02

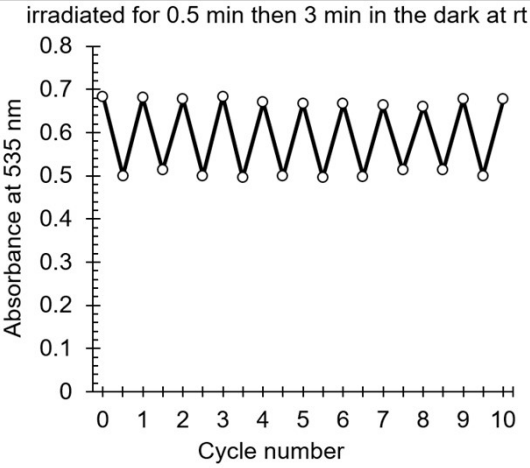

Fig. 22. Cyclicity of photochromic transformation of compound **1** at pH 7.99

5. Kinetics of dark relaxation of compounds 1 at different pH

($C = 2.5 \times 10^{-5}$ M, phosphate buffer, 20 °C)

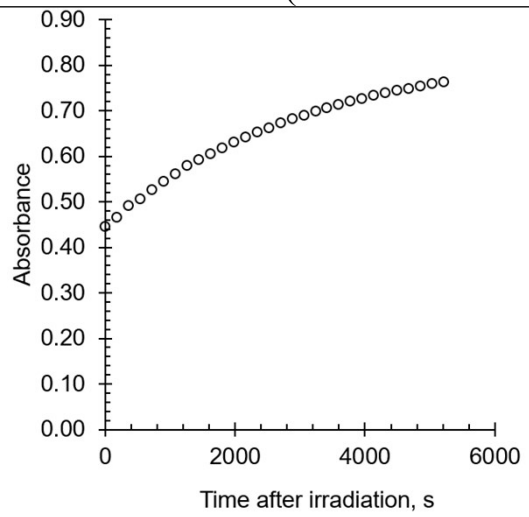

Fig. 23. Kinetics of the reverse thermal transformation for the compound **1 at** pH 2.08

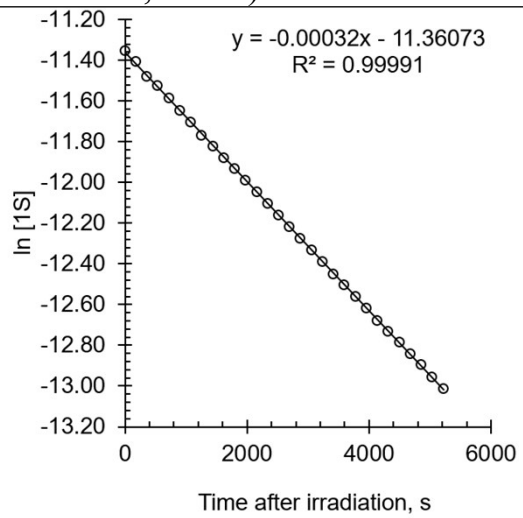

Fig. 24. The plot of fitting the concentration of photo-induced form [**1S**] in a first-order kinetic equation at pH 2.08

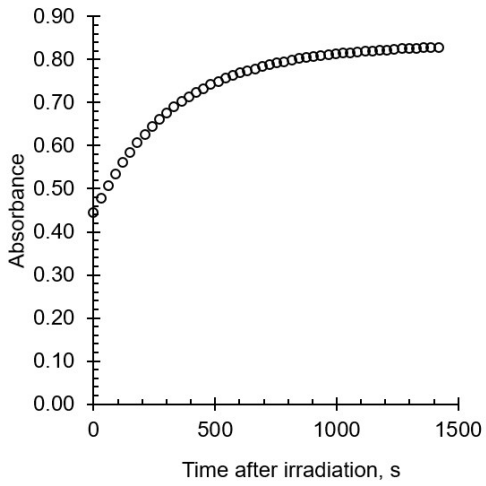

Fig. 23. Kinetics of the reverse thermal transformation for the compound **1 at** pH 3.08

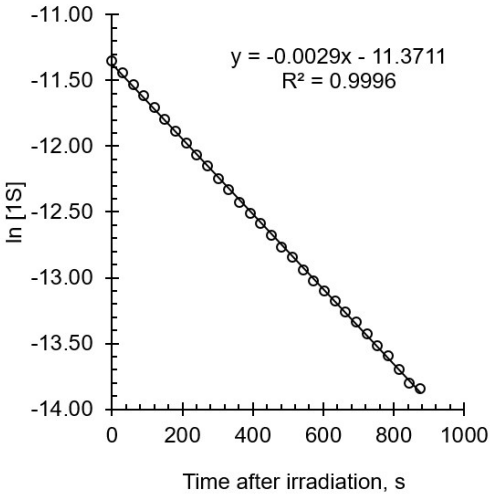

Fig. 25. The plot of fitting the concentration of photo-induced form [**1S**] in a first-order kinetic equation at pH 3.08

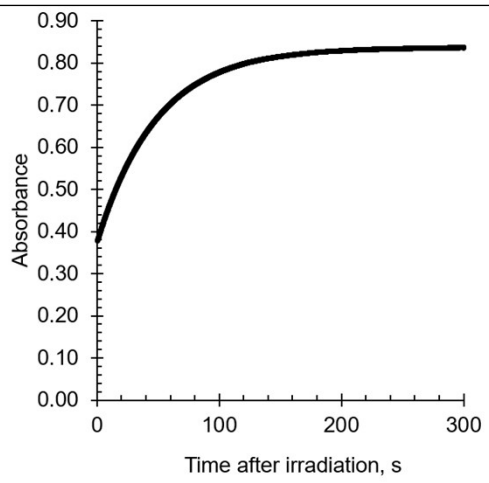

Fig. 26. Kinetics of the reverse thermal transformation for the compound **1 at** pH 4.08

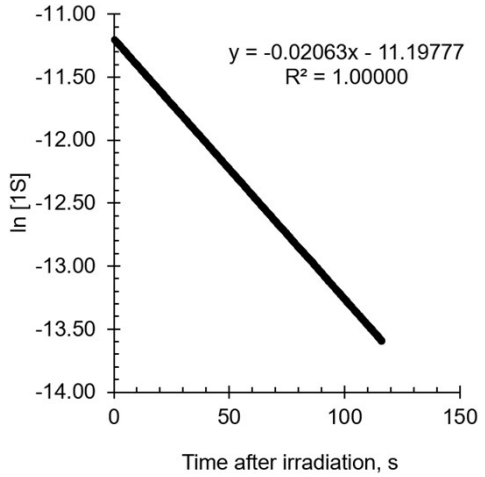

Fig. 27. The plot of fitting the concentration of photo-induced form [**1S**] in a first-order kinetic equation at pH 4.08

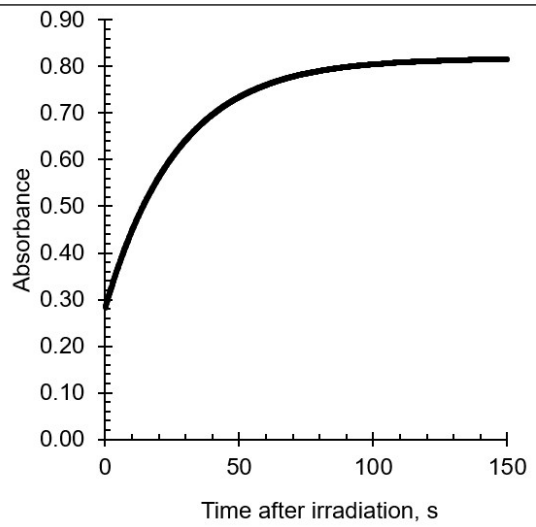

Fig. 28. Kinetics of the reverse thermal transformation for the compound **1 at** pH 4.54

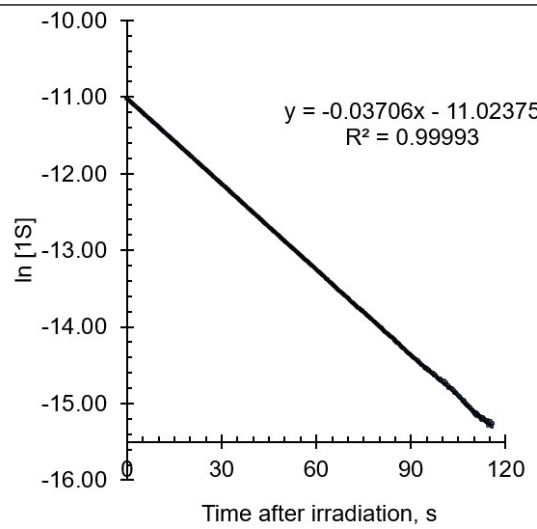

Fig. 29. The plot of fitting the concentration of photo-induced form [**1S**] in a first-order kinetic equation at pH 4.54

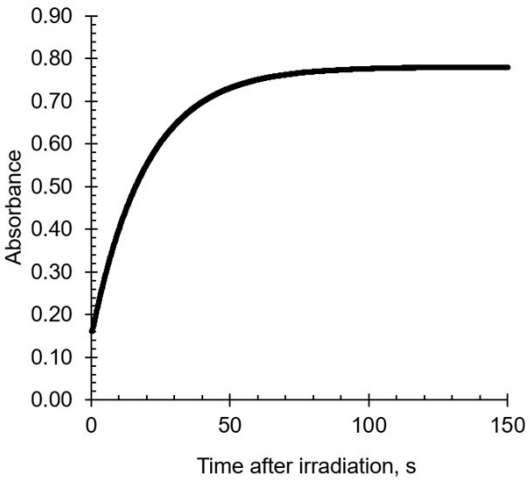

Fig. 30. Kinetics of the reverse thermal transformation for the compound **1 at** pH 5.03

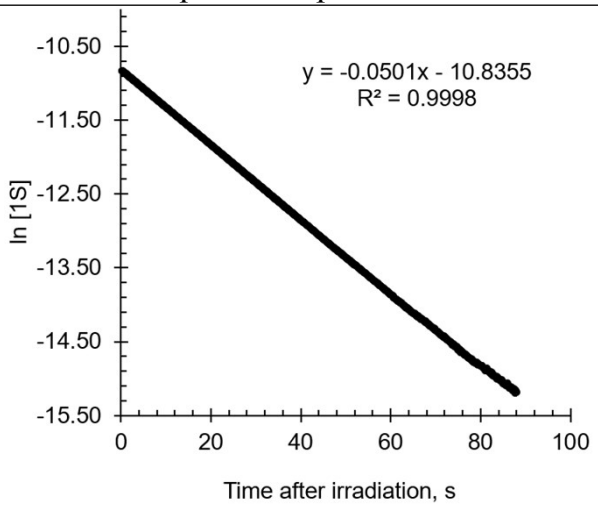

Fig. 31. The plot of fitting the concentration of photo-induced form [**1S**] in a first-order kinetic equation at pH 5.03

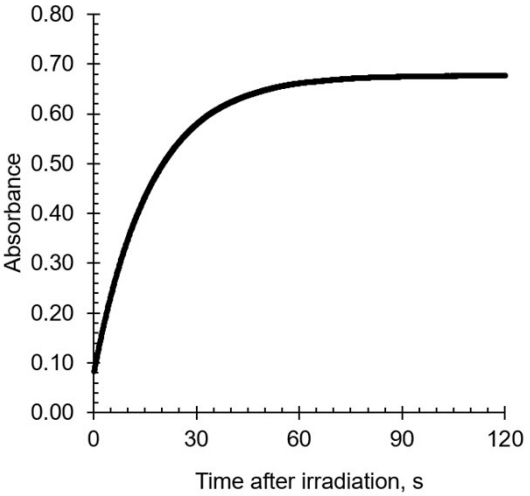

Fig. 32. Kinetics of the reverse thermal transformation for the compound **1 at** pH 6.03

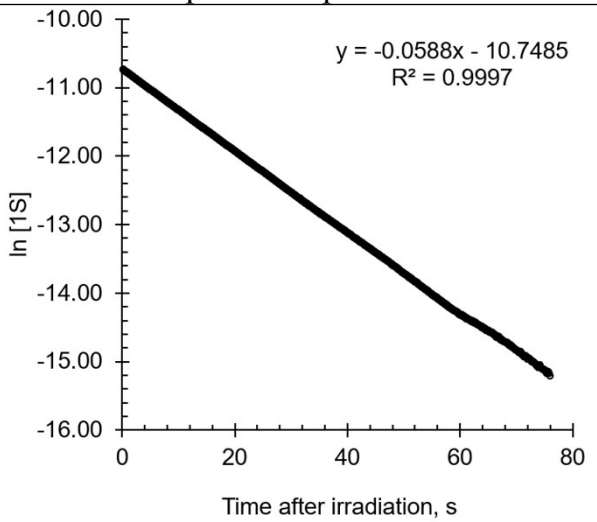

Fig. 33. The plot of fitting the concentration of photo-induced form [**1S**] in a first-order kinetic equation at pH 6.03

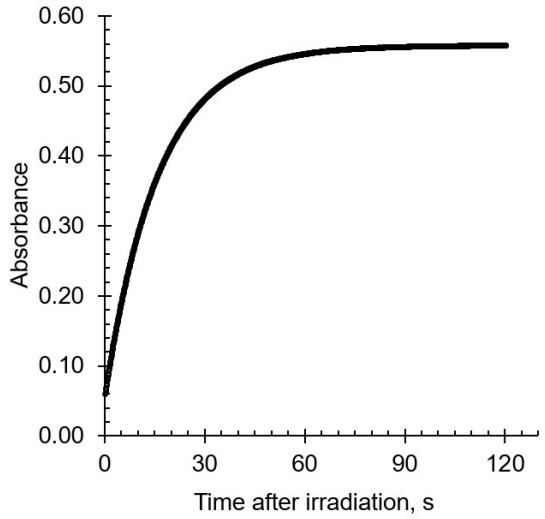

Fig. 34. Kinetics of the reverse thermal transformation for the compound **1 at** pH 6.50

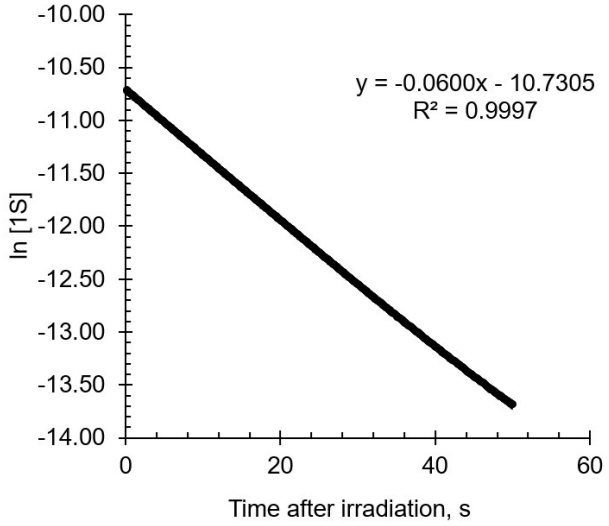

Fig. 35. The plot of fitting the concentration of photo-induced form [**1S**] in a first-order kinetic equation at pH 6.50

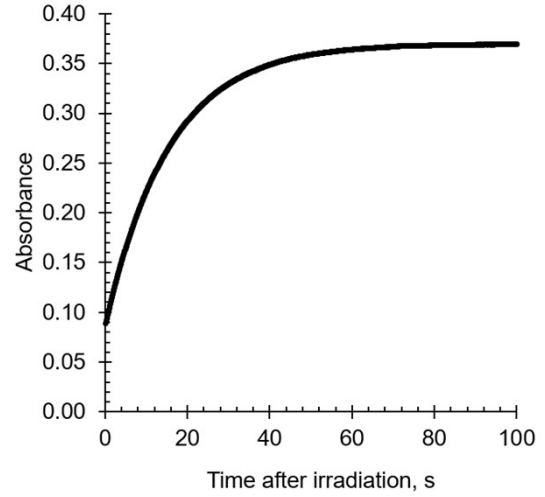

Fig. 36. Kinetics of the reverse thermal transformation for the compound **1 at** pH 7.02

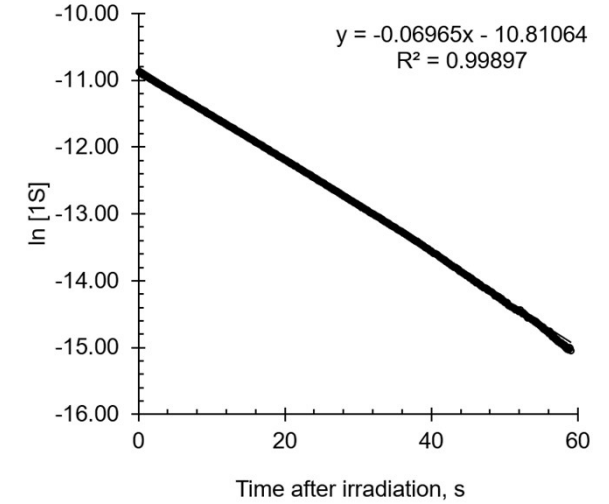

Fig. 37. The plot of fitting the concentration of photo-induced form [**1S**] in a first-order kinetic equation at pH 7.02

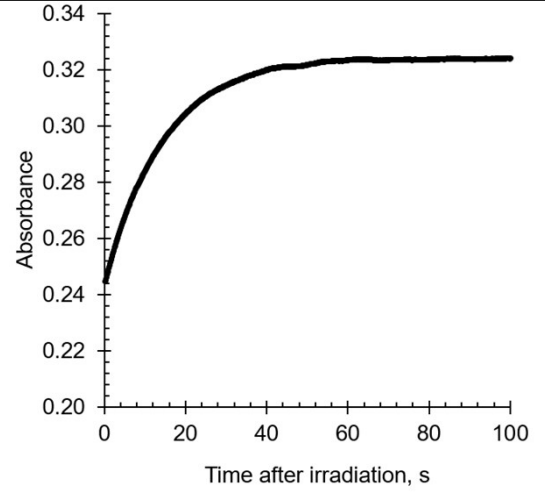

Fig. 38. Kinetics of the reverse thermal transformation for the compound **1 at** pH 7.99

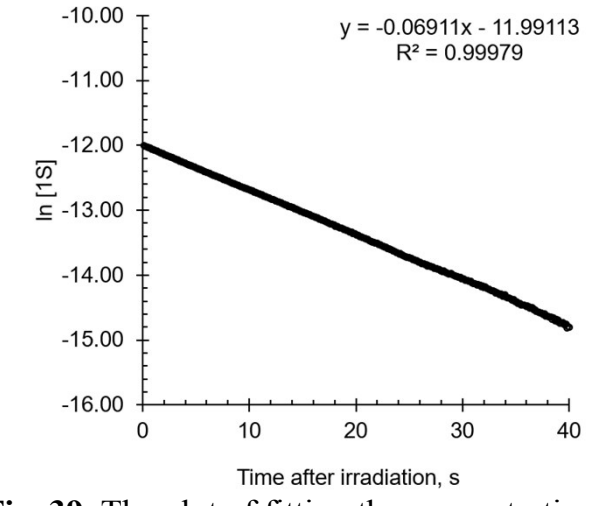

Fig. 39. The plot of fitting the concentration of photo-induced form [**1S**] in a first-order kinetic equation at pH 7.99

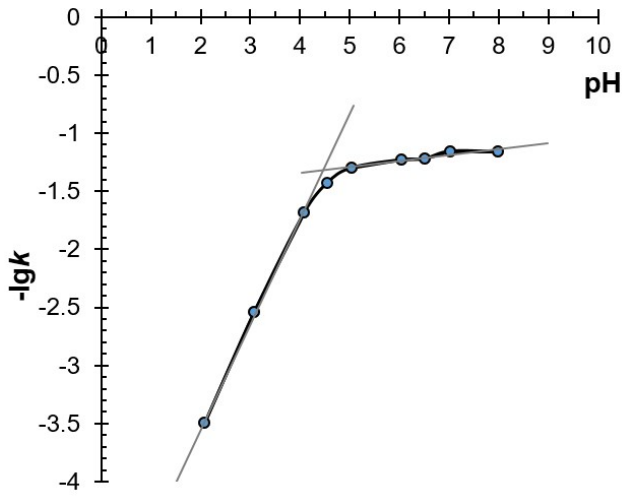

Fig. 40. Dependence of the negative logarithm of the dark reaction **1S** to **1** rate constant on pH value ($C = 2.5 \times 10^{-5}$ M, 20 °C)

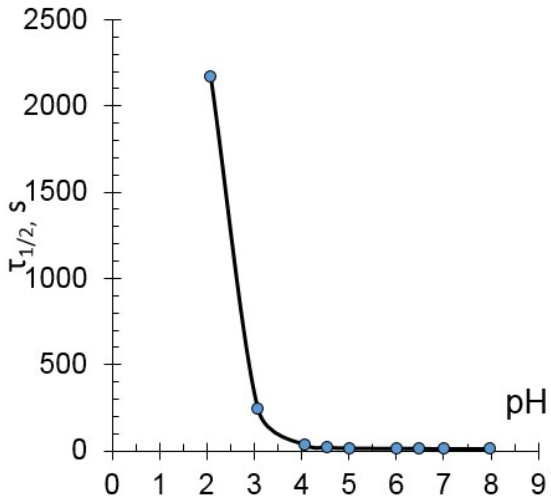

Fig. 41. Dependence of **1S** half-life period on pH value ($C = 2.5 \times 10^{-5}$ M, 20 °C)

6. Determination of acidity constant photoinduced form pK_a^{1S} in water and pH changes of aqueous solution of photoacid 1 after irradiation

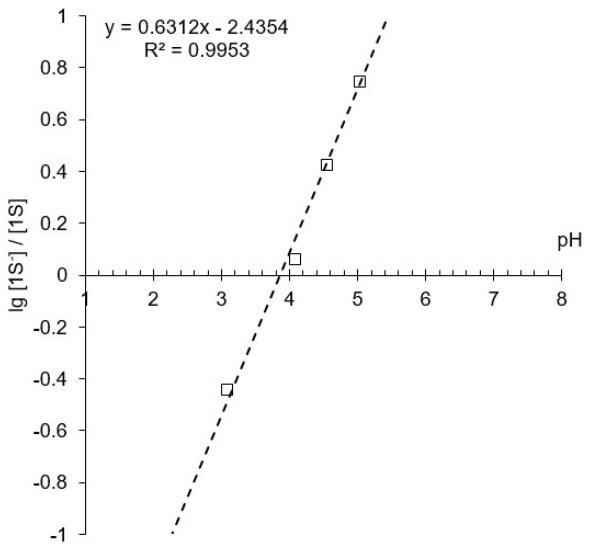

Fig. 42. Linear regression of logarithmic absorbance ratio of **1S** and **1S**$^-$ forms vs. pH ($C = 2.5 \times 10^{-5}$ M, 20°C)

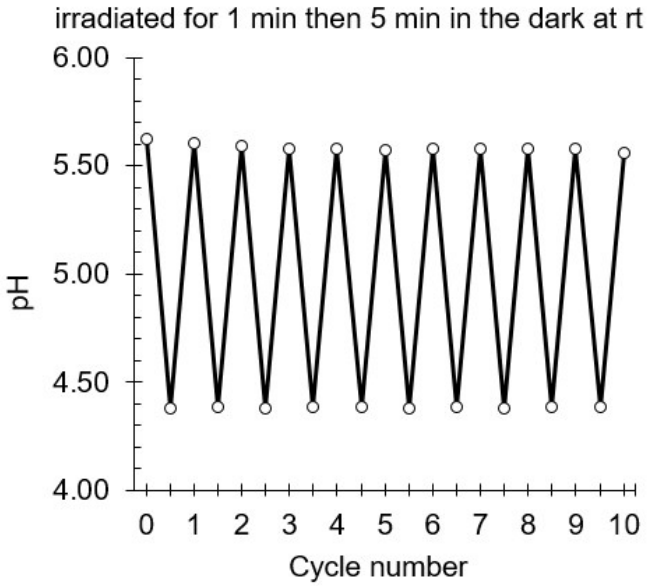

Fig. 43. pH changes of aqueous solution of photoacid **1** upon sequential irradiation with visible light and keeping in the dark (H_2O, $C = 1.0 \times 10^{-4}$ M, 20 °C)

7. NMR ^{1}H, ^{13}C spectra

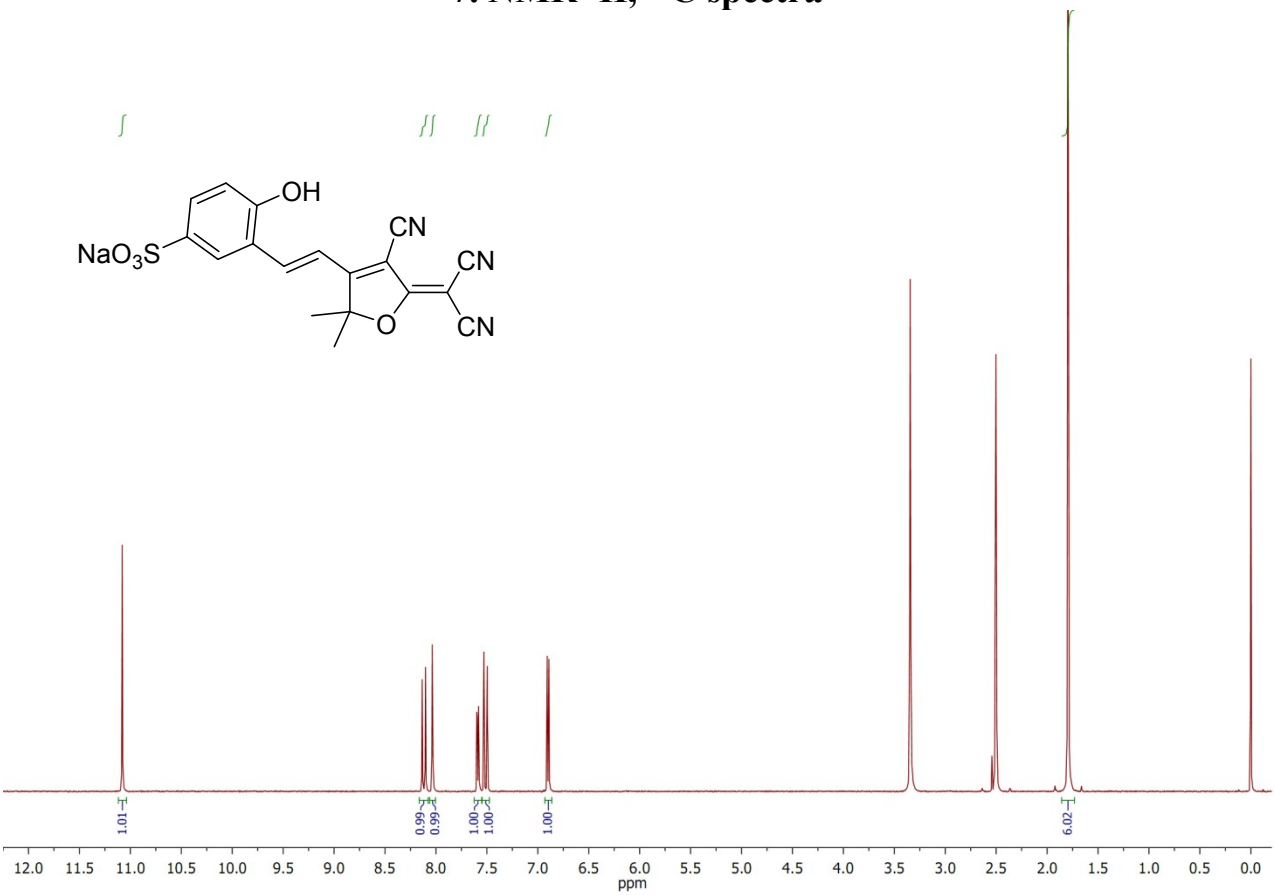

Fig. 44. ^{1}H-NMR-spectrum of compound **1** (500 MHz, DMSO−d_6, 293K)

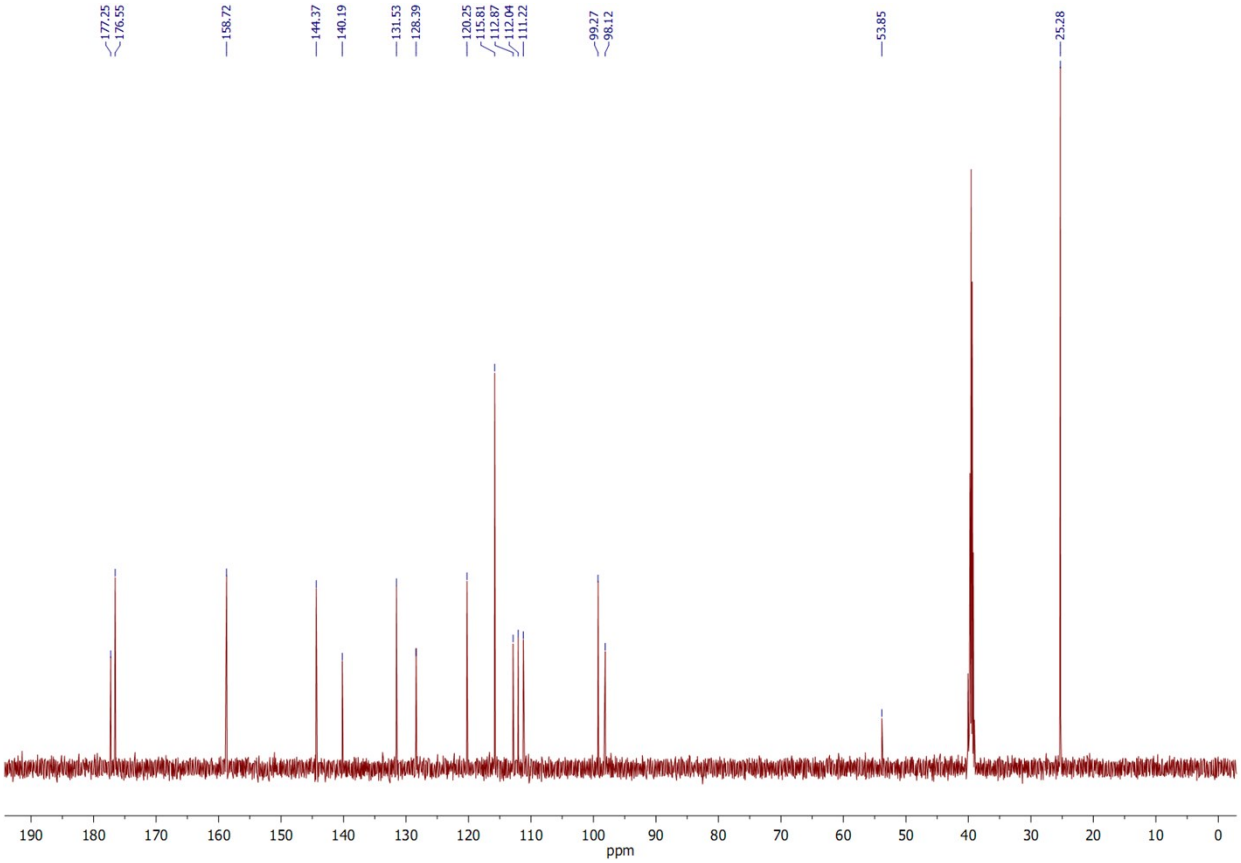

Fig. 45. ^{13}C-NMR-spectrum of compound **1** (126 MHz, DMSO−d_6, 296K)

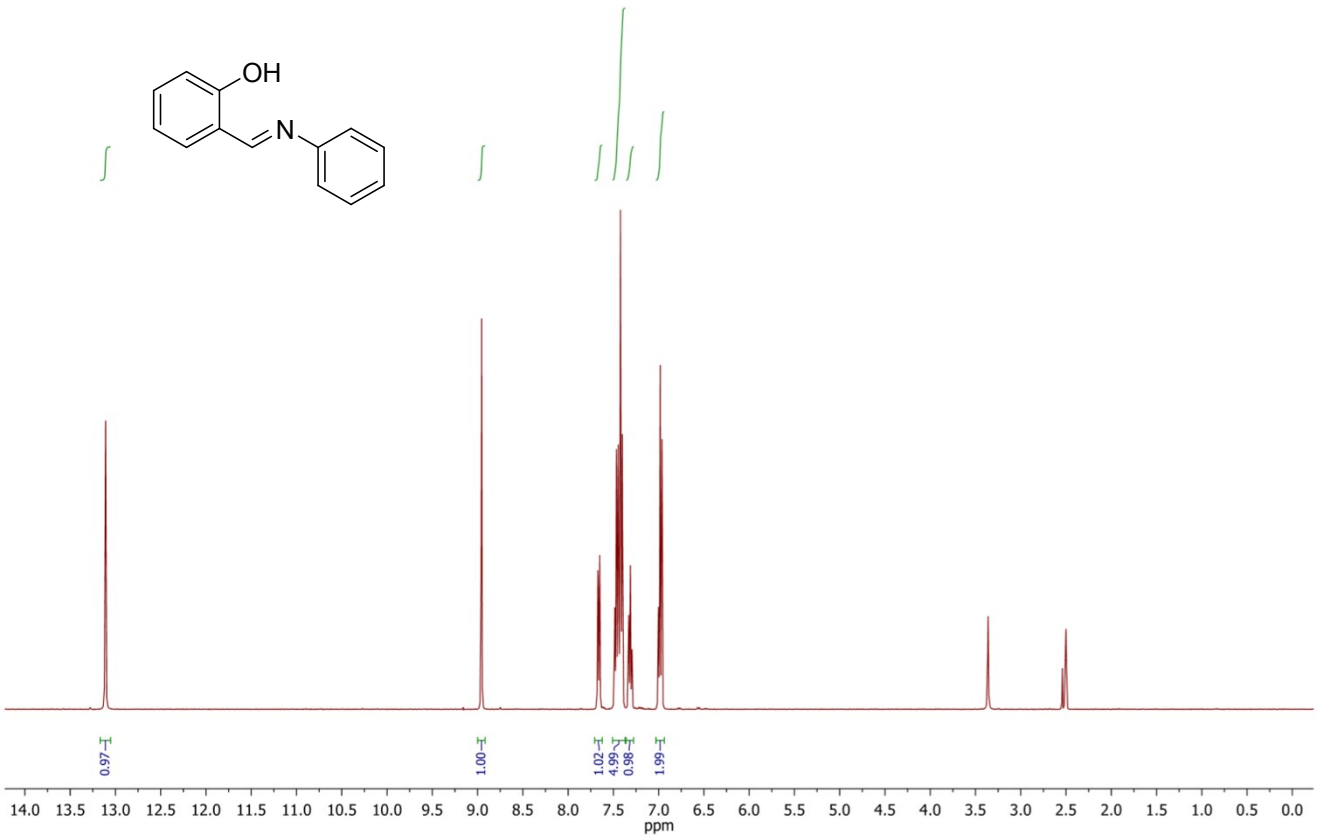

Fig. 46. ^{1}H-NMR-spectrum of compound **2** (400 MHz, DMSO−d_6, 293K)

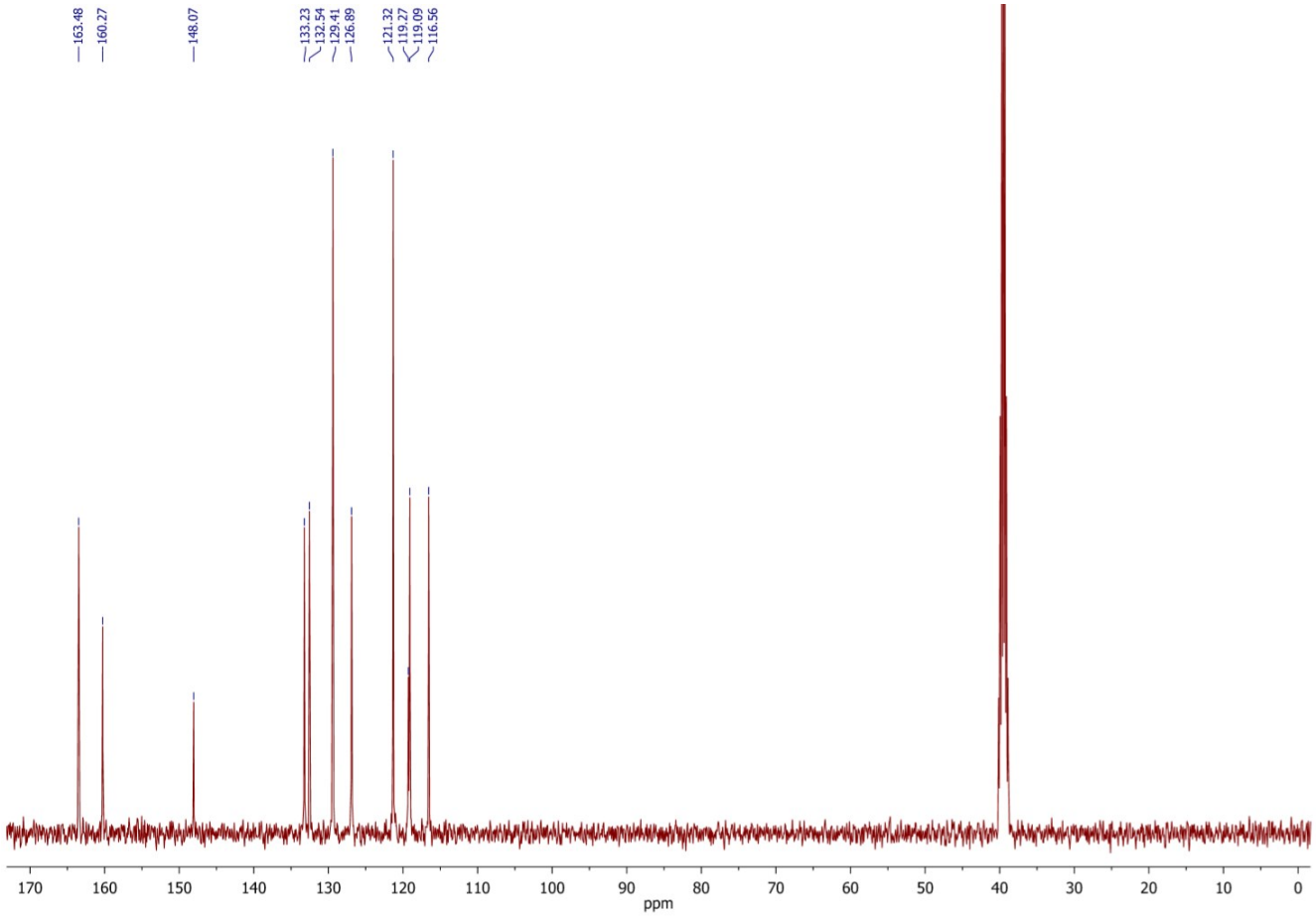

Fig. 47. ^{13}C-NMR-spectrum of compound **2** (100 MHz, DMSO−d_6, 296K)

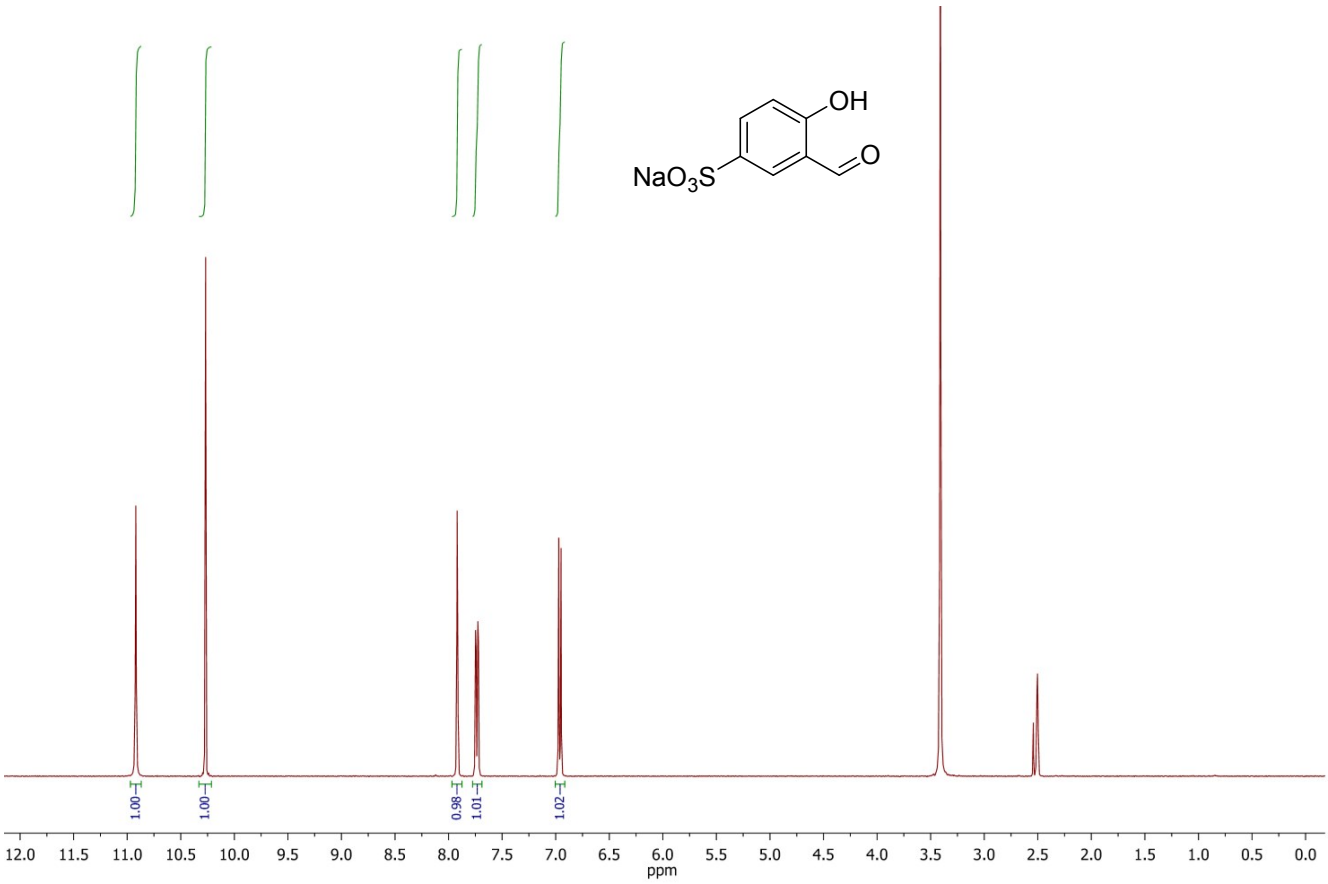

Fig. 48. ^{1}H-NMR-spectrum of compound **4** (400 MHz, DMSO−d_6, 293K)

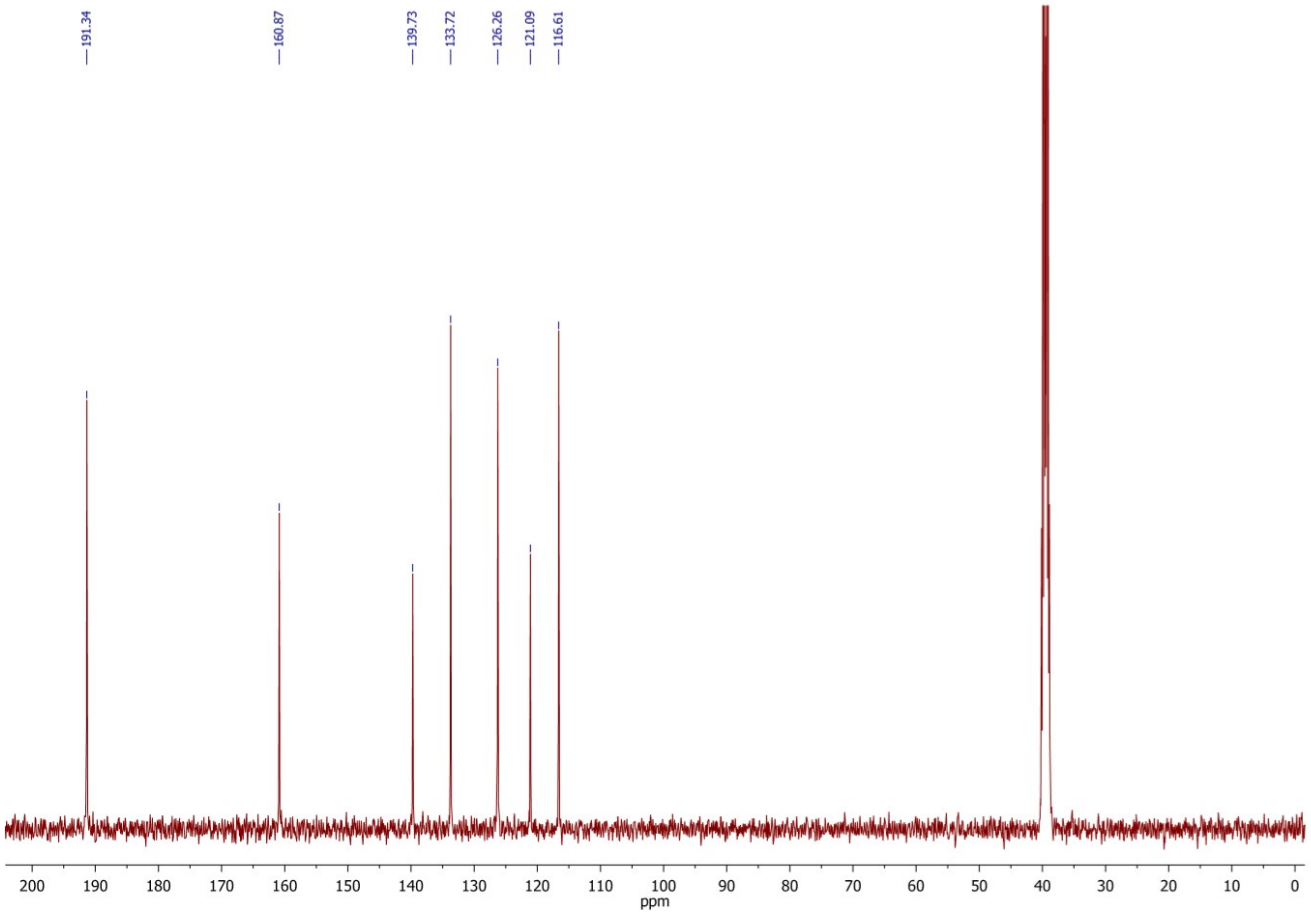

Fig. 49. ^{13}C-NMR-spectrum of compound **4** (100 MHz, DMSO−d_6, 296K)

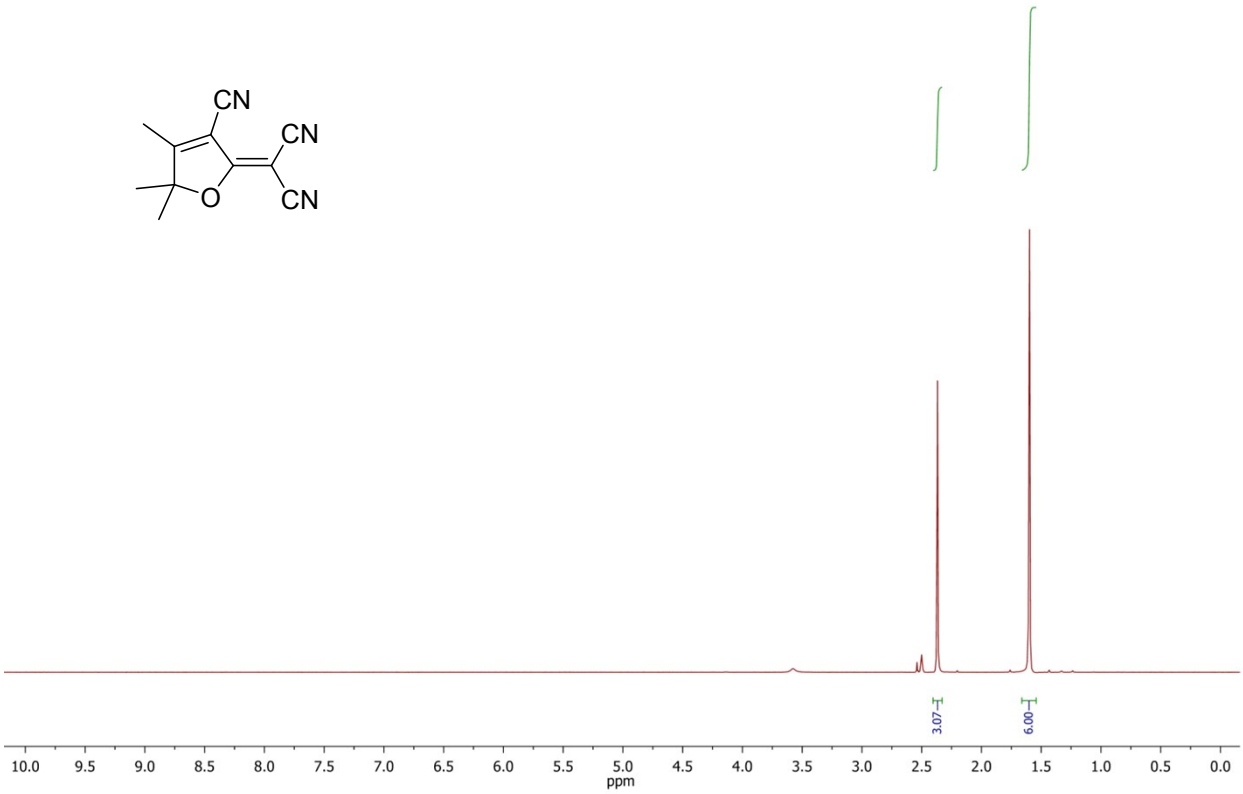

Fig. 50. ^{1}H-NMR-spectrum of compound **TCF** (400 MHz, DMSO−d_6, 293K)

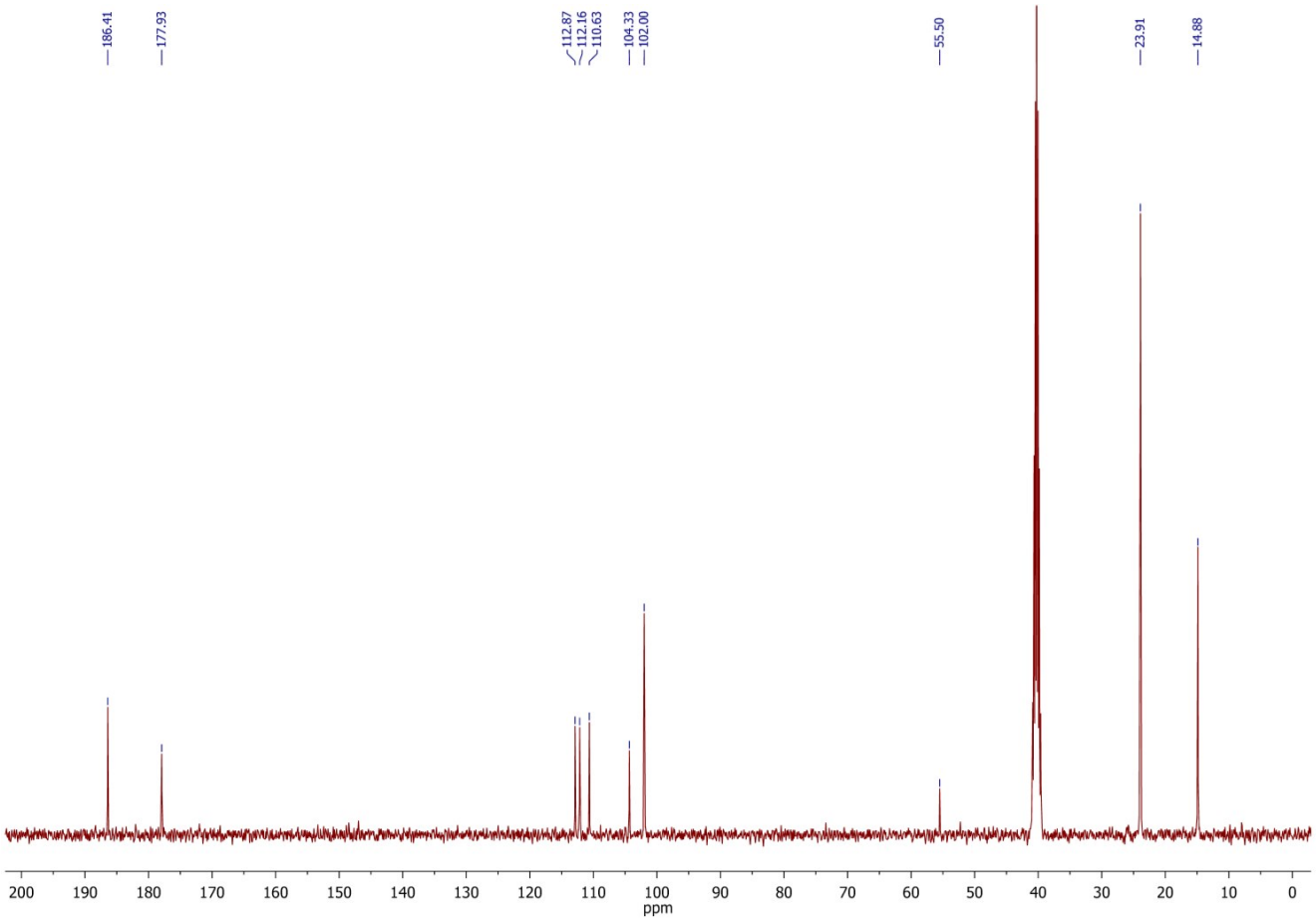

Fig. 51. ^{13}C-NMR-spectrum of compound **TCF** (100 MHz, DMSO−d_6, 293K)

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