

New indoline spiropyrans with highly stable merocyanine forms

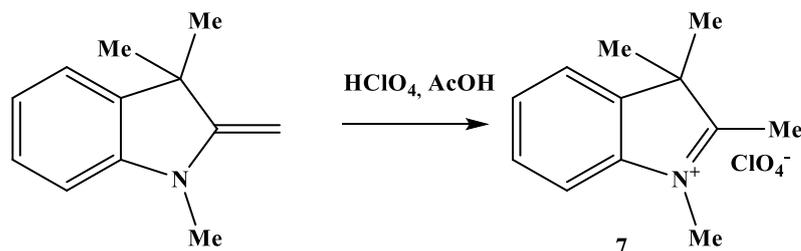
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Experimental part

A) Materials and methods

All starting reagents (Alfa Aesar and Merck) were used as purchased. Organic solvents were purified and dried according to standard methods. NMR spectra were recorded on a Bruker AVANCE-600 (600 MHz) spectrometer. The signals were assigned relative to the signals of residual protons of DMSO- d_6 ($\delta^H = 2.50$ ppm) or $CDCl_3$ ($\delta^H = 7.26$ ppm). IR spectra were recorded on a Varian Excalibur 3100 FT-IR spectrometer using a partial internal reflection method. Electronic absorption spectra and kinetic curves were recorded on an Agilent-8453 spectrophotometer equipped with the thermostatic cell. The irradiation of solutions with the filtered light of a high-pressure Hg lamp was performed on a Newport 66902 equipment. Acetonitrile and toluene of the spectroscopic grade (Aldrich) was used to prepare solutions. HRMS were registered on a Bruker UHR-TOF MaxisTM Impact instrument (electrospray ionization, in MeCN solution, using $HCO_2Na-HCO_2H$ for calibration). Elemental analysis was carried out using the classical microanalysis method [N. E. Gel'man, E. A. Terent'eva, T. M. Shanina, L. M. Kiparenko, *Metody kolichestvennogo organicheskogo elementnogo analiza (Methods of Quantitative Organic Elemental Analysis)*, Khimiya, Moscow, 1987. (in Russian)]. Melting points were determined on a Fisher-Jones apparatus "Fisher Scientific".

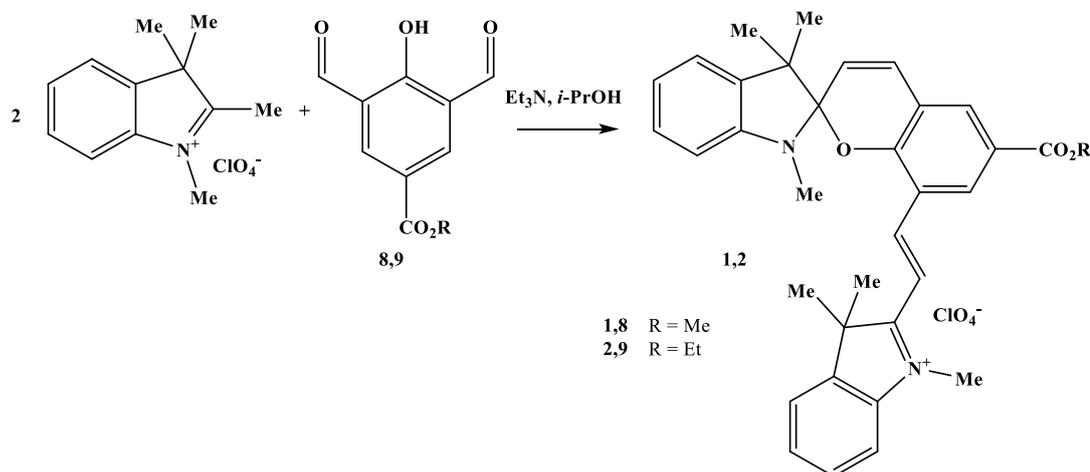
B) Synthesis of initial compounds



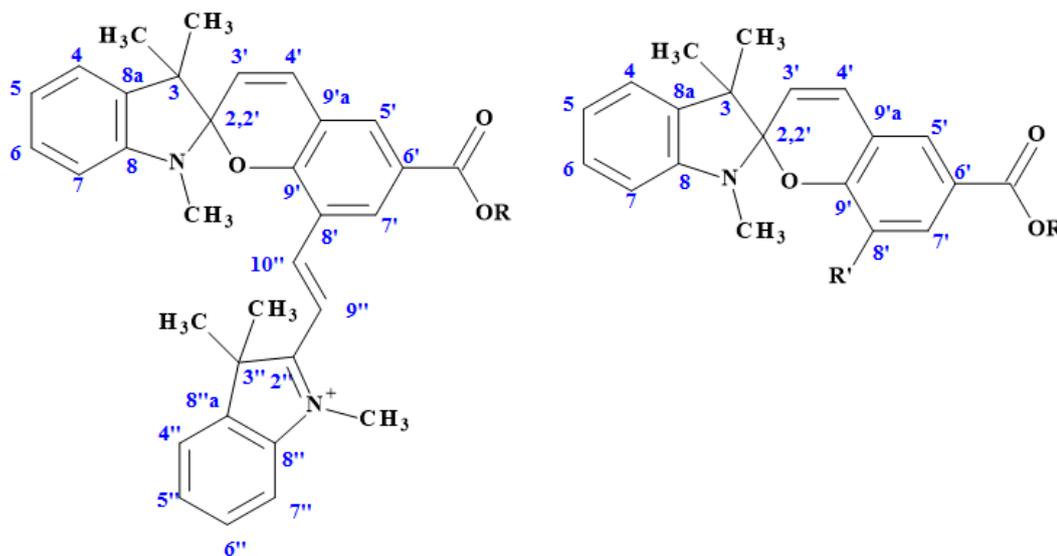
1,2,3,3-Tetramethyl-3H-indolium perchlorate 7. Perchloric acid (1.2 ml) was added dropwise to a solution of 1,3,3-trimethylindoline (2.5 ml) in Et_2O (15 ml) in an ice bath, then it was left to cool overnight until a precipitate forms. The precipitate was recrystallized from acetic acid with the addition of one drop of $HClO_4$, filtered and washed with diethyl ether. A yellow crystalline substance was obtained and used further without identification, yield 63%.

Aldehydes **8-11** were prepared as reported [A. K. Gupta, A. Dhir, C. P. Pradeep, *Eur. J. Org. Chem.*, 2015, 122–129. A. V. Laptev, A. Y. Lukin, N. E. Belikov, K. V. Zvezdin, O. V. Demina, V. A. Barachevsky, S. D. Varfolomeev, A. A. Khodonov, V. I. Shvets, *Russ. Chem. Bull., Int. Ed.*, 2014, **63**, 2026 (*Izv. AN, Ser. Khim.*, 2014, **9**, 2026)].

C) Synthesis of cationic derivatives of spiropyrans



Scheme S2. Synthesis of cationic spiropyrans



Scheme S3. Scheme of atoms labeling in the NMR spectra

2-[(*E*)-2-(6-Methoxycarbonyl-1',3',3'-trimethyl-1',3'-dihydrospiro[chromene-2,2'-indol]-8-yl)vinyl]-1,3,3-trimethyl-3*H*-indolium perchlorate **1**. 1,2,3,3-Tetramethyl-3*H*-indol-1-ium perchlorate **7** (1.641 g, 6 mmol) was added to a solution of aldehyde **8** (0.624 g, 3 mmol) in propan-2-ol (20 ml). Then triethylamine (0.42 ml) was carefully added dropwise. The mixture was refluxed for 6 h. Most of the solvent was evaporated, and the residue was left overnight at room temperature for the precipitate forming. The precipitate was filtered off and purified by column chromatography on silica gel using chloroform as eluent. After recrystallization from

ethanol, dark green crystals were obtained. Yield 0.752 g (40%). mp 217 °C. IR, ν , cm^{-1} : 1718 (C=O), 1608 (C=O), 1481 (C=C), 1463 (C=C), 1096 (ClO_4^-), 927 ($\text{C}_{\text{spiro-O}}$). HRMS (ESI): m/z $[\text{M}]^+$ calcd for $\text{C}_{34}\text{H}_{35}\text{N}_2\text{O}_3$: 519.2642; found: 519.2645. Calculated, %: C – 65.96; H – 5.70; Cl – 5.73; N – 4.52. $\text{C}_{34}\text{H}_{35}\text{ClN}_2\text{O}_7$. Found, %: C – 65.46; H – 5.83; Cl – 5.60; N – 4.57.

Spiro form (SP). NMR ^1H (DMSO- d_6) δ , ppm.: 8.60 (d, $J = 2.0$ Hz, 1H, H-7'), 8.09 – 7.98 (m, 2H, H-10'', H-5'), 7.87 – 7.79 (m, 1H, H-7''), 7.72 – 7.68 (m, 1H, H-4'), 7.62 – 7.44 (m, 3H, H-9'', H-5'', H-6''), 7.28 (d, $J = 10.4$ Hz, 1H, H-4'), 7.24 – 7.16 (m, 2H, H-6, H-4), 6.91 (td, $J = 7.7, 0.7$ Hz, 1H, H-5), 6.69 (d, $J = 7.7$ Hz, 1H, H-7), 6.05 (d, $J = 10.4$ Hz, 1H, H-3'), 3.86 (s, 3H, O- CH_3), 3.58 (s, 3H, N^+ - CH_3), 2.70 (s, 3H, N- CH_3), 1.35 (s, 3H, C- CH_3), 1.34 (s, 3H, C- CH_3), 1.24 (s, 3H, C- CH_3), 1.16 (s, 3H, C- CH_3).

NMR ^{13}C (DMSO- d_6) δ , ppm.: 182.4 (C-2''), 165.7 (CO_2CH_3), 158.2 (C-9'), 147.7 (C-8), 146.7 (C-10''), 143.9 (C-8''), 136.2 (C-8a), 133.6 (C-7'), 132.7 (C-5'), 130.0 (C-6''), 129.5 (C-4'), 129.4 (C-5'), 128.5 (C-6), 123.1 (C-4''), 122.9 (C-9a'), 122.3 (C-4), 120.9 (C-3'), 120.7 (C-8'), 120.5 (C-5), 120.4 (C-6'), 115.7 (C-7''), 114.9 (C-9''), 108.4 (C-2,2'), 108.0 (C-7), 52.7 (O- CH_3), 52.4 (C-3), 52.3 (C-3''), 34.3 (N^+ - CH_3), 29.2 (N- CH_3), 25.9 (C- CH_3), 25.8 (C- CH_3), 25.7 (C- CH_3), 20.1 (C- CH_3).

Merocyanine form (MC). NMR ^1H (DMSO- d_6) δ , ppm.: 8.48 (s, 2H, H-5', H-7'), 8.45 (d, $J = 15.6$ Hz, 2H, H-4', H-10''), 8.29 (d, $J = 15.6$ Hz, 2H, H-3', H-9''), 7.75 (m, 4H, H-4, H-4'', H-7, H-7''), 7.62 – 7.44 (m, 4H, H-5, H-6, H-5'', H-6''), 3.94 (s, 6H, N^+ - CH_3), 3.81 (s, 3H, O- CH_3), 1.74 (s, 12H, C- CH_3).

NMR ^{13}C (DMSO- d_6) δ , ppm.: 182.2 (C-2,2', C-2''), 179.7 (C-6'), 166.4 (CO_2CH_3), 153.5 (C-4', C-10''), 143.4 (C-8'', C-8), 142.5 (C-8a'', C-8a), 142.0 (C-5', C-7'), 129.2 (C-5, C-5''), 128.4 (C-6, C-6''), 126.5 (C-9'), 123.1 (C-7, C-7''), 114.4 (C-4, C-4''), 113.1 (C-9'a, C-8'), 109.0 (C-3', C-9''), 52.0 (C-3, C-3''), 51.6 (O- CH_3), 33.8 (N^+ - CH_3), 26.9 (*gem*-C- CH_3).

2-[(*E*)-2-(6-Ethoxycarbonyl-1',3',3'-trimethyl-1',3'-dihydrospiro[chromene-2,2'-indol]-8-yl)vinyl]-1,3,3-trimethyl-3*H*-indolium perchlorate **2**. 1,2,3,3-Tetramethyl-3*H*-indol-1-ium perchlorate **7** (1.094 g, 4 mmol) was added to a solution of aldehyde **9** (0.444 g, 2 mmol) in propan-2-ol (20 ml). Then triethylamine (0.28 ml) was carefully added dropwise. The mixture was refluxed for 11 h. Most of the solvent was evaporated, and the product was precipitated by treatment with water-ethanol mixture (20:1). The precipitate was filtered off and recrystallized from ethanol. Dark green crystals were obtained. Yield 0.605 g (49%), mp 245°C. IR, ν , cm^{-1} : 1711 (C=O), 1608 (C=O), 1456 (C=C), 1094 (ClO_4^-), 927 ($\text{C}_{\text{spiro-O}}$). HRMS (ESI): m/z $[\text{M}]^+$ calcd for $\text{C}_{35}\text{H}_{37}\text{N}_2\text{O}_3$: 533.2799; found: 533.2796. Calculated, %: C – 66.40; H – 5.89; Cl – 5.60; N – 4.42. $\text{C}_{35}\text{H}_{37}\text{N}_2\text{O}_7\text{Cl}$. Found, %: C – 65.93; H – 6.01; N – 4.32; Cl – 5.56.

Spiro form (SP). NMR ^1H (DMSO- d_6) δ , ppm.: 8.60 (d, $J = 2.0$ Hz, 1H, H-7'), 8.08 (dd, $J = 9.3, 7.3$ Hz, 2H, H-10'', H-5'), 7.92 – 7.81 (m, 1H, H-7''), 7.75 – 7.66 (m, 1H, H-4''), 7.64 – 7.46 (m, 2H, H-5'', H-6''), 7.52 (d, $J = 16.6$ Hz, 1H, H-9''), 7.31 (d, $J = 10.4$ Hz, 1H, H-4'), 7.26 – 7.20 (m, 2H, H-6, H-4), 6.93 (t, $J = 7.4$ Hz, 1H, H-5), 6.72 (d, $J = 7.7$ Hz, 1H, H-7), 6.08 (d, $J = 10.4$ Hz, 1H, H-3'), 4.36 (q, $J = 7.1$ Hz, 2H, CH_2 - CH_3), 3.60 (s, 3H, N^+ - CH_3), 2.72 (s, 3H, N- CH_3), 1.38 (s, 3H, *gem*-C- CH_3), 1.37 (s, 3H, *gem*-C- CH_3), 1.36 – 1.33 (m, 3H, CH_2 - CH_3), 1.27 (s, 3H, *gem*-C- CH_3), 1.18 (s, 3H, *gem*-C- CH_3).

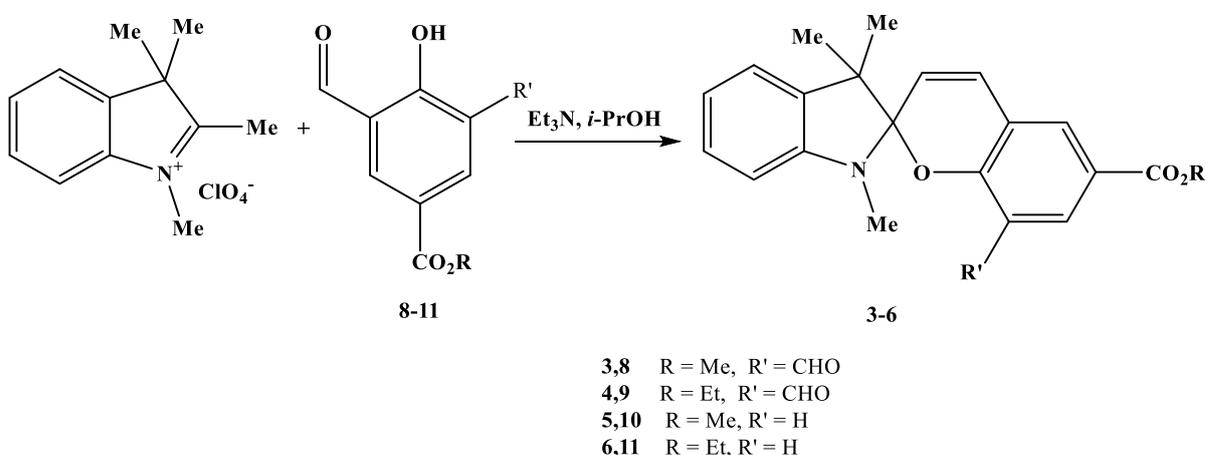
NMR ^{13}C (DMSO- d_6) δ , ppm.: 181.9 (C-2''), 164.7 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 157.7 (C-9'), 147.2 (C-8), 146.2 (C-10''), 143.4 (C-8''), 141.9 (C-8'a), 135.7 (C-8a), 133.1 (C-7'), 132.1 (C-5'), 129.5 (C-

6''), 129.0 (C-5''), 128.9 (C-4'), 127.9 (C-6), 122.6 (C-9'a, C-4''), 121.8 (C-4), 120.4 (C-3'), 120.0 (C-8'), 119.9 (C-5), 115.2 (C-7''), 114.4 (C-9''), 107.8 (C-2,2'), 107.5 (C-7), 60.8 ($\underline{\text{CH}_2\text{-CH}_3}$), 51.8 (C-3), 51.7 (C-3''), 33.8 (N⁺-CH₃), 28.6 (N-CH₃), 25.3 (*gem*-C- $\underline{\text{CH}_3}$), 25.2 (CH₂- $\underline{\text{CH}_3}$), 19.6 (*gem*-C- $\underline{\text{CH}_3}$), 14.2 (*gem*-C- $\underline{\text{CH}_3}$).

Merocyanine form (MC). NMR ¹H (DMSO-*d*₆) δ , ppm.: 8.52 – 8.43 (m, 4H, H-3', H-9'', H-5', H-7'), 8.32 (d, *J* = 15.5 Hz, 4H, H-4', H-10''), 7.81 – 7.75 (m, 4H, H-4, H-4'', H-7, H-7''), 7.64 – 7.46 (m, 4H, H-5'', H-6'', H-5, H-6), 4.33 – 4.29 (m, 2H, $\underline{\text{CH}_2\text{-CH}_3}$), 3.97 (s, 6H, N⁺-CH₃), 1.36 – 1.33 (m, 3H, $\underline{\text{CH}_2\text{-CH}_3}$) 1.77 (s, 12H, *gem*-C-CH₃).

NMR ¹³C (DMSO-*d*₆) δ , ppm.: 181.7 (C-2,2', C-2''), 165.4 ($\underline{\text{CO}_2\text{CH}_2\text{CH}_3}$) 152.9 (C-4', C-10''), 142.8 (C-8'', C-8''a, C-8, C-8a), 141.5 (C-7', C-5'), 122.6 (C-9', C-9'a, C-8', C-7, C-7''), 120.2 (C-5'', C-6'', C-5, C-6), 113.9 (C-4, C-4''), 108.6 (C-3', C-9''), 60.0 ($\underline{\text{CH}_2\text{-CH}_3}$), 51.1 (C-3, C-3''), 33.2 (N⁺-CH₃), 26.3 (*gem*-C- $\underline{\text{CH}_3}$), 25.4 (CH₂- $\underline{\text{CH}_3}$),

D) Synthesis of spiropyrans without cationic fragments



Scheme S4. Synthesis of spiropyrans without cationic fragments

Methyl 8-formyl-1',3',3'-trimethyl-1',3'-dihydrospiro[chromene-2,2'-indole]-6-carboxylate **3**. 1,2,3,3-Tetramethyl-3*H*-indol-1-ium perchlorate **7** (0.820 g, 3 mmol) was added to a solution of aldehyde **8** (0.624 g, 3 mmol) in propan-2-ol (15 ml). Then triethylamine (0.28 ml) was carefully added dropwise. The mixture was boiled for 15 min. After extraction of the target compound with chloroform from a water-alcohol medium, it was purified on a chromatographic column with silica gel using chloroform as an eluent. Crystallized from *n*-hexane. Pink powder was obtained. Yield 0.316 g (29%), mp 148°C. IR, ν , cm⁻¹: 1722 (C=O), 1686 (C=O), 1586 (C=C), 939 (C_{spiro}-O). NMR ¹H (CDCl₃) δ , ppm.: 10.09 (s, 1H, CHO), 8.31 (d, *J* = 2.1 Hz, 1H, H-7'), 7.95 (d, *J* = 2.1 Hz, 1H, H-5'), 7.16 (t, *J* = 7.7 Hz, 1H, H-6), 7.05 (d, *J* = 7.2 Hz, 1H, H-4), 6.95 (d, *J* = 10.4 Hz, 1H, H-4'), 6.85 (t, *J* = 7.4 Hz, 1H, H-5), 6.53 (d, *J* = 7.5 Hz, 1H, H-7), 5.86 (d, *J* = 10.4 Hz, 1H, H-3'), 3.88 (s, 3H, OCH₃), 2.75 (s, 3H, N-CH₃), 1.31 (s, 3H, -C-CH₃), 1.19 (s, 3H, -C-CH₃). NMR ¹³C (CDCl₃) δ , ppm.: 187.9 (CHO), 165.9 ($\underline{\text{CO}_2\text{CH}_3}$), 160.5 (C-6'), 147.4 (C-8), 135.9 (C-8a), 133.3 (C-5'), 129.8 (C-7'), 128.5 (C-4'), 127.8 (C-6), 122.3 (C-9'), 122.2 (C-9'a), 121.4 (C-4), 121.0 (C-3'), 120.2 (C-8'), 119.9 (C-5), 107.1 (C-7, C-2,2'), 52.3 (C-3), 52.1 (O-CH₃), 28.9 (N-CH₃), 25.8 (C- $\underline{\text{CH}_3}$), 20.3 (C- $\underline{\text{CH}_3}$). Calculated, %: C – 72.71, H – 5.82, N – 3.85, O – 17.61. C₂₂H₂₁NO₄. Found: C – 71.53, H – 5.98, N – 3.81.

Ethyl 8-formyl-1',3',3'-trimethyl-1',3'-dihydrospiro[chromene-2,2'-indole]-6-carboxylate **4**. 1,2,3,3-Tetramethyl-3*H*-indol-1-ium perchlorate **7** (0.820 g, 3 mmol) was added to a solution of aldehyde **9** (0.666 g, 3 mmol) in propan-2-ol (15 ml). Then triethylamine (0.42 ml) was added dropwise. The mixture was boiled for 15 min. After extraction of the target compound with chloroform from a water-alcohol mixture, it was purified on a chromatographic column with silica gel using chloroform as an eluent. Crystallized from *n*-hexane. Pink powder was obtained. Yield 0.475 g (42%), mp 137°C. IR, ν , cm^{-1} : 1712 (C=O), 1683 (C=O), 1584 (C=C), 928 ($\text{C}_{\text{spiro-O}}$). NMR ^1H (CDCl_3) δ , ppm.: 10.09 (s, 1H, CHO), 8.31 (d, $J = 2.1$ Hz, 1H, H-7'), 7.96 (d, $J = 2.1$ Hz, 1H, H-5'), 7.16 (t, $J = 7.6$ Hz, 1H, H-6), 7.05 (d, $J = 7.2$ Hz, 1H, H-4), 6.95 (d, $J = 10.4$ Hz, 1H, H-4'), 6.86 (t, $J = 7.4$ Hz, 1H, H-5), 6.53 (d, $J = 7.7$ Hz, 1H, H-7), 5.85 (d, $J = 10.4$ Hz, 1H, H-3'), 4.34 (q, $J = 7.1$ Hz, 2H, $\text{CH}_2\text{-CH}_3$), 2.75 (s, 3H, N- CH_3), 1.36 (t, $J = 7.1$ Hz, 3H, $\text{CH}_2\text{-CH}_3$), 1.31 (s, 3H, *gem*-C- CH_3), 1.20 (s, 3H, *gem*-C- CH_3). NMR ^{13}C (CDCl_3) δ , ppm.: 188.1 (CHO), 165.5 (C-7'), 160.5 (C-6'), 147.5 (C-8), 136.0 (C-8a), 133.3 (C-5'), 129.71 ($\text{CO}_2\text{C}_2\text{H}_5$), 128.6 (C-4'), 127.8 (C-6), 122.6 (C-4), 122.3 (C-9'), 121.4 (C-9'a), 120.9 (C-3'), 120.1 (C-8'), 119.9 (C-5), 107.1 (C-7), 61.1 ($\text{CH}_2\text{-CH}_3$), 52.3 (C-3), 28.9 (N- CH_3), 25.8 (*gem*-C- CH_3), 20.3 (*gem*-C- CH_3), 14.3 ($\text{CH}_2\text{-CH}_3$). Calculated, %: C – 73.19; H – 6.14; N – 3.71; O – 16.96. $\text{C}_{23}\text{H}_{23}\text{NO}_4$. Found, %: C – 73.09; H – 6.27; N – 3.69.

Methyl 1',3',3'-trimethyl-1',3'-dihydrospiro[chromene-2,2'-indole]-6-carboxylate **5**. 1,2,3,3-Tetramethyl-3*H*-indolium perchlorate **7** (0.547 g, 2 mmol) was added to a solution of aldehyde **10** (0.360 g, 2 mmol) in propan-2-ol (15 ml). Then triethylamine (0.28 ml) was added dropwise. The mixture was boiled for 15 min. After extraction of the target compound with chloroform from a water-alcohol mixture, it was recrystallized from ethanol. Pink powder was obtained. Yield 0.469 g (70%), mp 109°C. NMR ^1H (CDCl_3) δ , ppm.: 7.78 (dd, $J = 8.5, 2.1$ Hz, 1H, H-7'), 7.76 (d, $J = 2.1$ Hz, 1H, H-5'), 7.17 (td, $J = 7.7, 1.0$ Hz, 1H, H-6) 7.06 (d, $J = 7.1$ Hz, 1H, H-4), 6.88 (d, $J = 10.3$ Hz, 1H, H-4'), 6.85 (t, $J = 7.4$ Hz, 1H, H-5), 6.71 (d, $J = 8.5$ Hz, 1H, H-8'), 6.52 (d, $J = 7.7$ Hz, 1H, H-7), 5.73 (d, $J = 10.3$ Hz, 1H, H-3'), 3.86 (s, 1H, -O- CH_3), 2.72 (s, 3H, N- CH_3), 1.27 (s, 3H, C- CH_3), 1.16 (s, 3H, C- CH_3). NMR ^{13}C (CDCl_3) δ , ppm.: 166.7, 158.5, 148.0, 136.5, 131.6, 129.0, 128.6, 127.7, 122.1, 121.5, 120.1, 119.4, 118.5, 115.0, 106.9, 105.3, 52.0, 51.8, 29.7, 28.8, 25.9, 20.0.

Ethyl 1',3',3'-trimethyl-1',3'-dihydrospiro[chromene-2,2'-indole]-6-carboxylate **6**. 1,2,3,3-Tetramethyl-3*H*-indol-1-ium perchlorate **7** (0.547 g, 2 mmol) was added to a solution of aldehyde **11** (0.389 g, 2 mmol) in propan-2-ol (15 ml). Then triethylamine (0.28 ml) was added dropwise. The mixture was boiled for 15 min. After extraction of the target compound with chloroform from a water-alcohol mixture, it was recrystallized from ethanol. Pink powder was obtained. Yield 0.466 g (69%), mp 103°C. NMR ^1H (CDCl_3) δ , ppm.: 7.79 (dd, $J = 8.5, 2.2$ Hz, 1H, H-7'), 7.77 (d, $J = 2.1$ Hz, 1H, H-5'), 7.20 – 7.13 (m, 1H, H-6), 7.06 (dd, $J = 7.2, 1.0$ Hz, 1H, H-4), 6.89 (d, $J = 10.3$ Hz, 1H, H-4'), 6.84 (t, $J = 7.4$ Hz, 1H, H-5), 6.71 (d, $J = 8.5$ Hz, 1H, H-8'), 6.52 (d, $J = 7.7$ Hz, 1H, H-7), 5.73 (d, $J = 10.3$ Hz, 1H, H-3'), 4.33 (q, $J = 7.1$ Hz, 2H, $\text{CH}_2\text{-CH}_3$), 2.72 (s, 3H, N- CH_3), 1.36 (t, $J = 7.1$ Hz, 3H, $\text{CH}_2\text{-CH}_3$), 1.28 (s, 3H, C- CH_3), 1.16 (s, 3H, C- CH_3). NMR ^{13}C (CDCl_3) δ , ppm.: 166.2, 158.4, 148.0, 136.5, 131.6, 129.0, 128.6, 127.7, 122.4, 121.5, 120.0, 119.4, 118.4, 114.9, 106.9, 105.3, 60.6, 51.9, 29.7, 28.8, 20.0, 14.4.

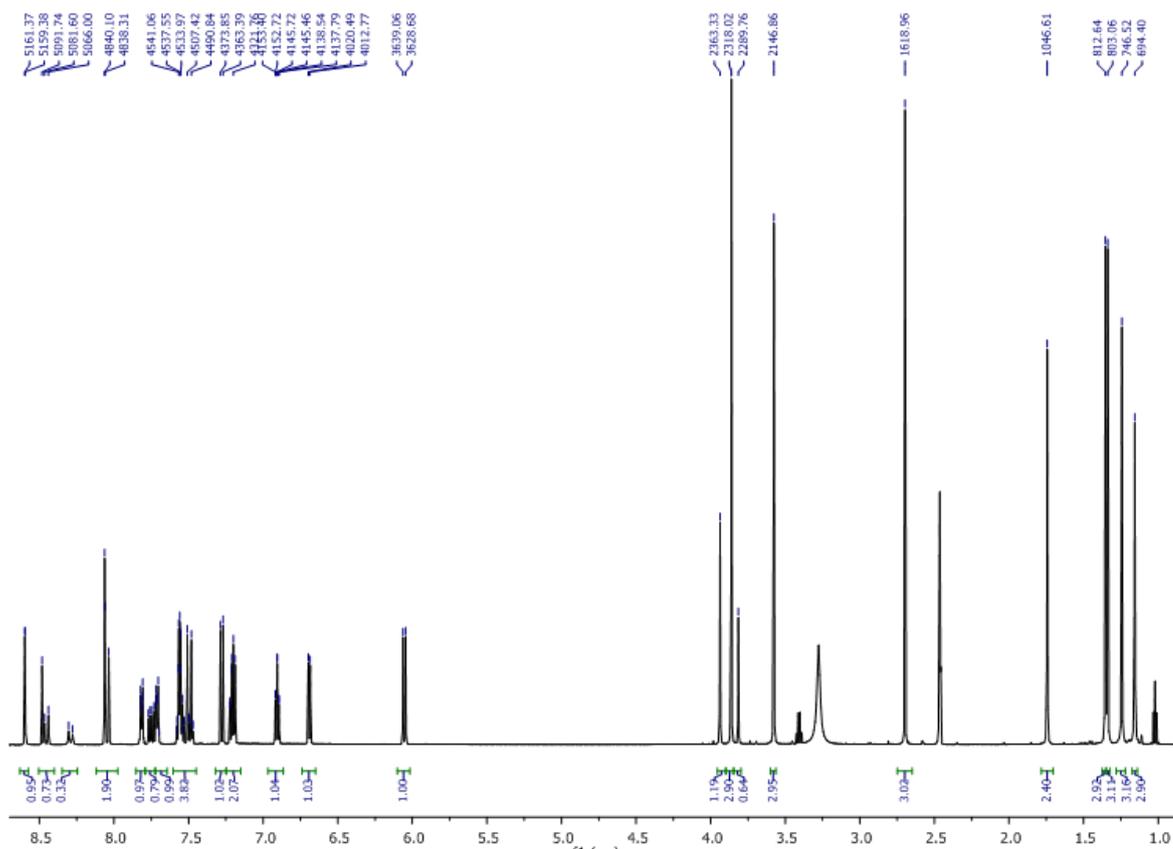


Figure S1. NMR ^1H spectrum of compound **1**, general view

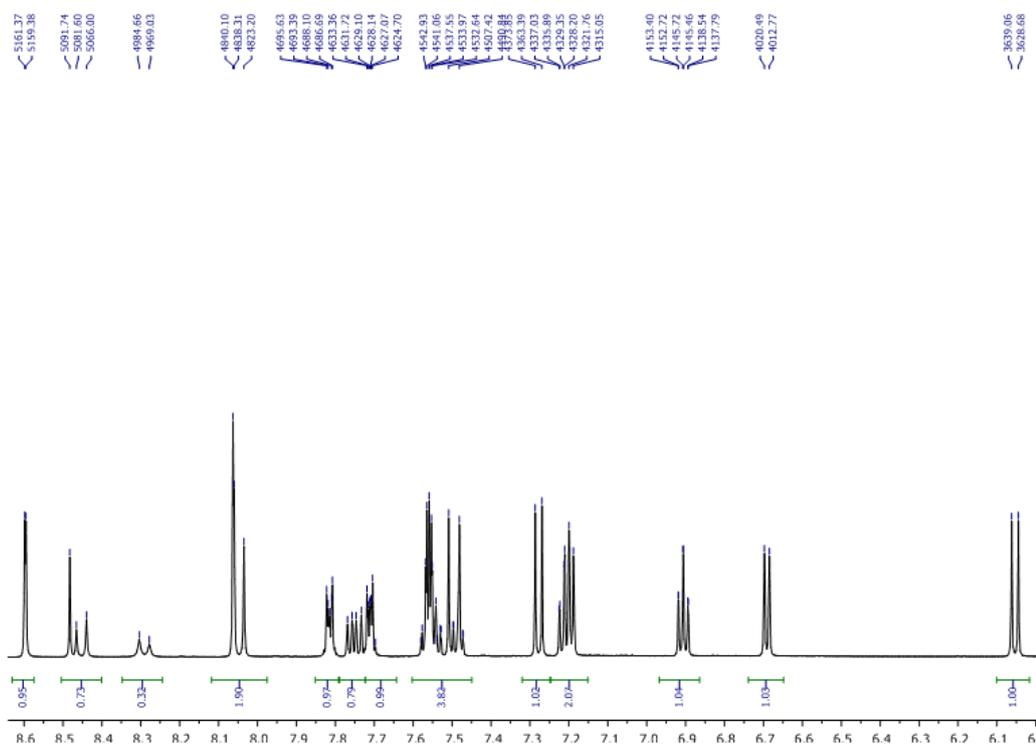


Figure S2. NMR ^1H spectrum of compound **1**, aromatic proton region

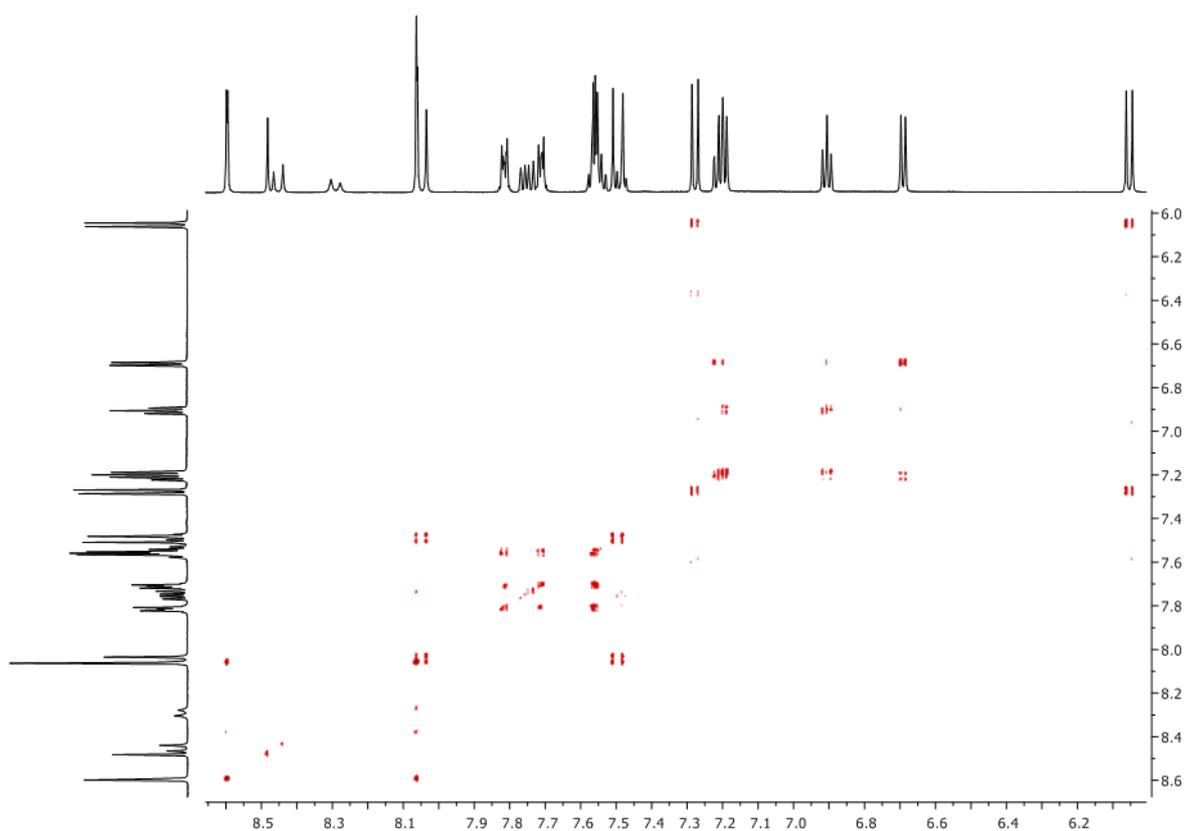


Figure S3. COSY ^1H - ^1H NMR spectrum of compound **1**, aromatic proton region

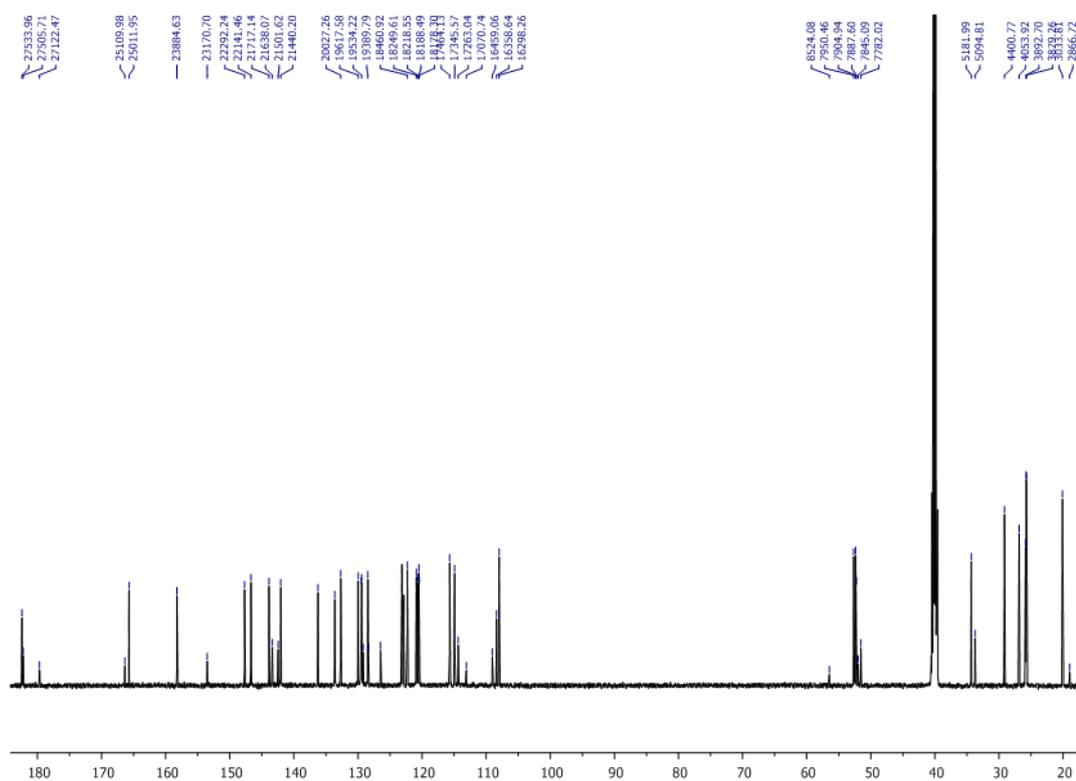


Figure S4. NMR ^{13}C spectrum of compound **1**

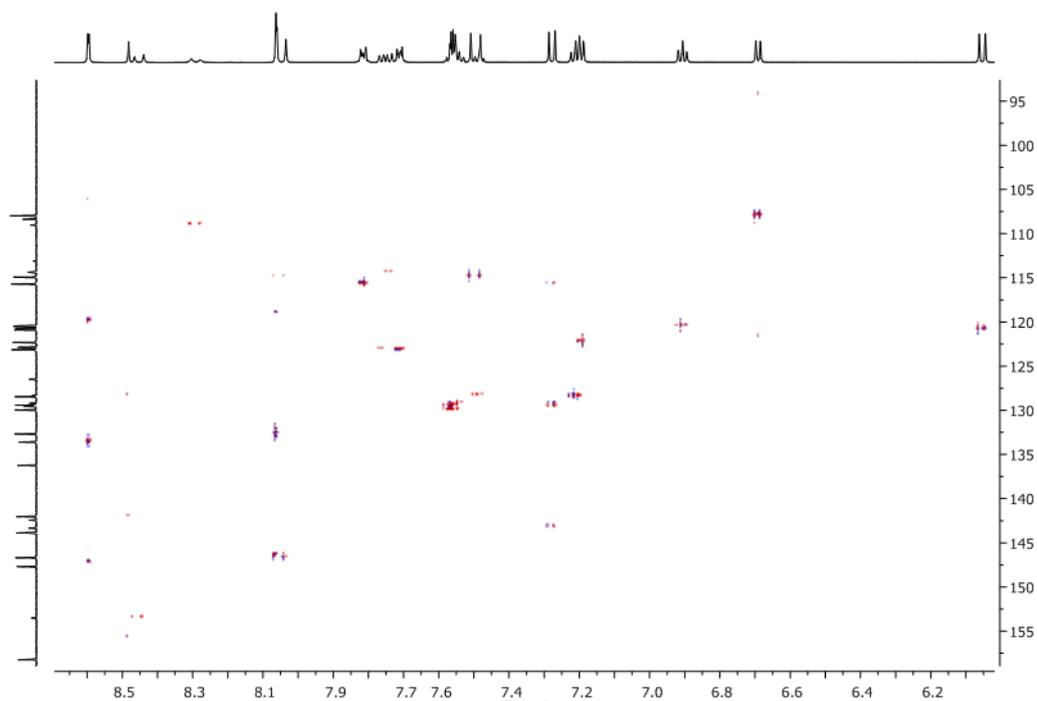


Figure S5. HSQC ^1H - ^{13}C NMR spectrum of compound **1**, aromatic proton region

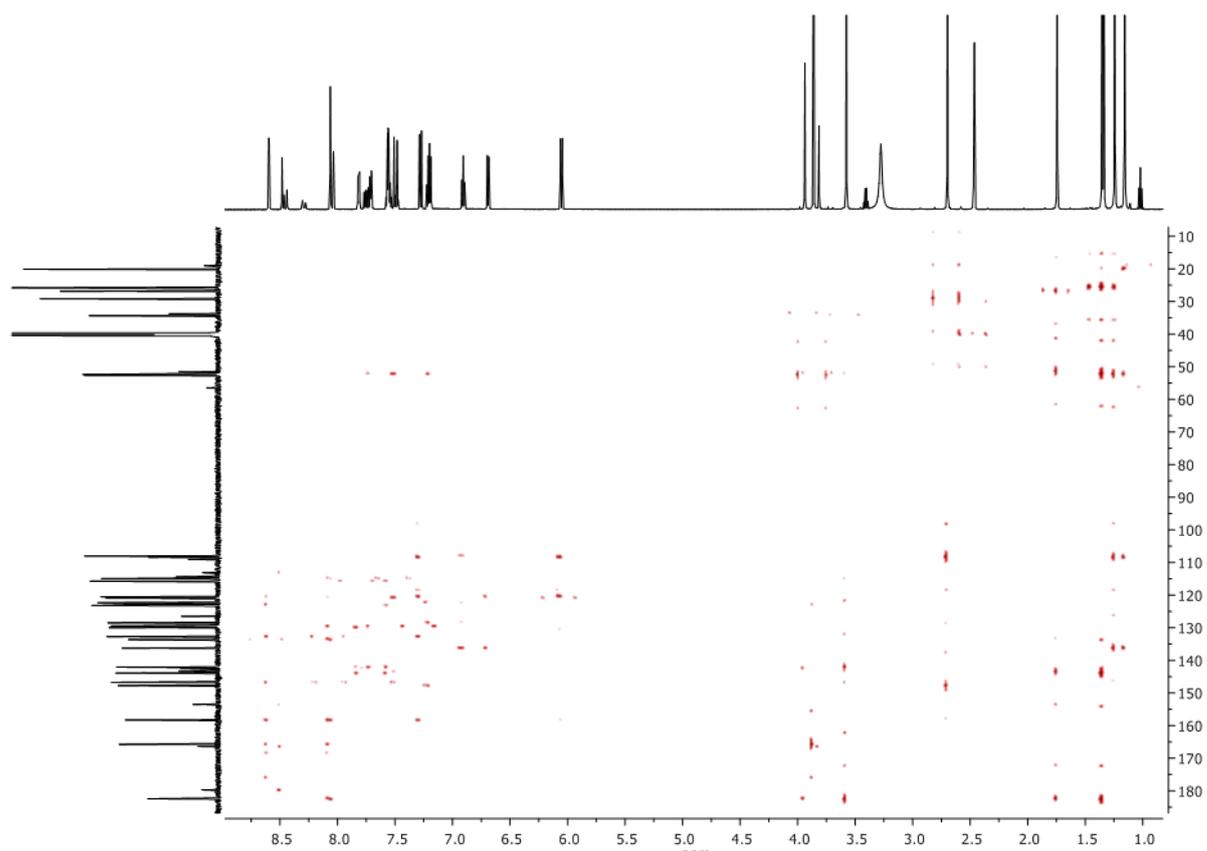


Figure S6. HMBC ^1H - ^{13}C NMR spectrum of compound **1**

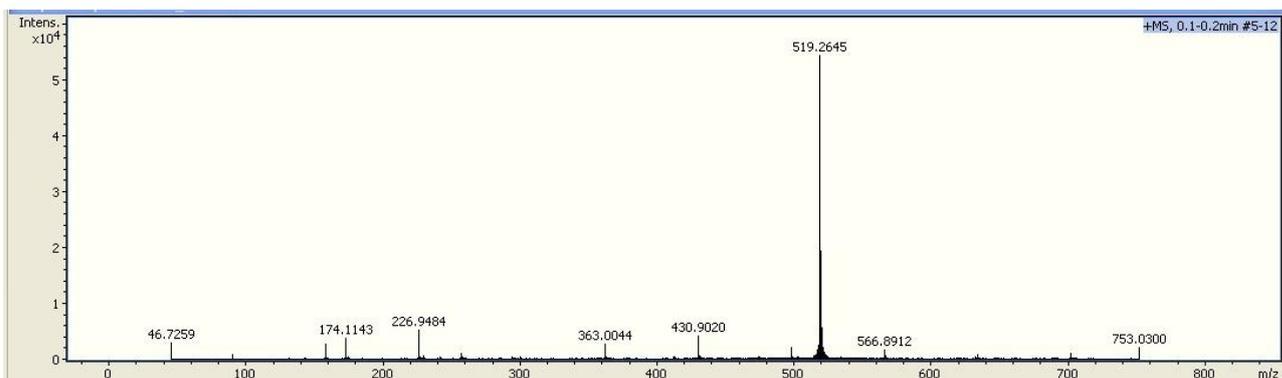


Figure S7. HRMS spectrum of compound 1

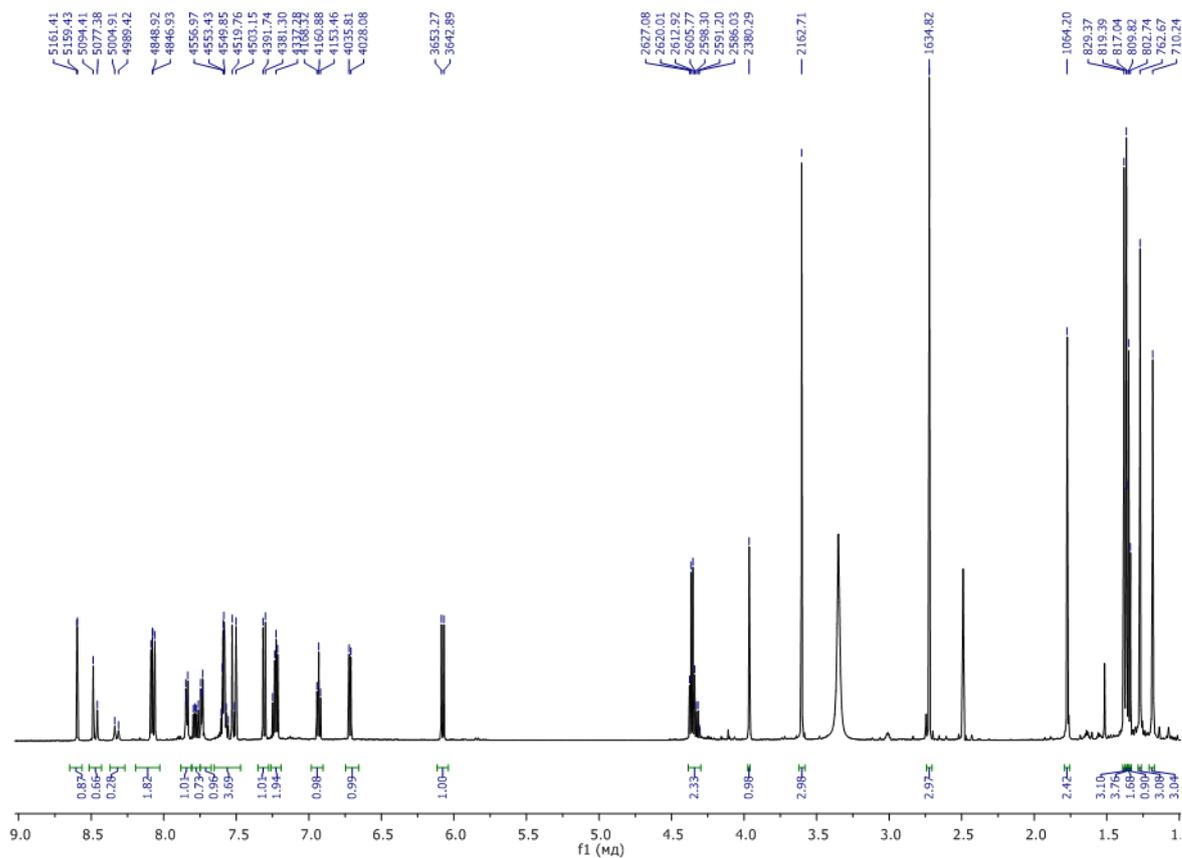


Figure S8. NMR ^1H spectrum of compound 2, general view

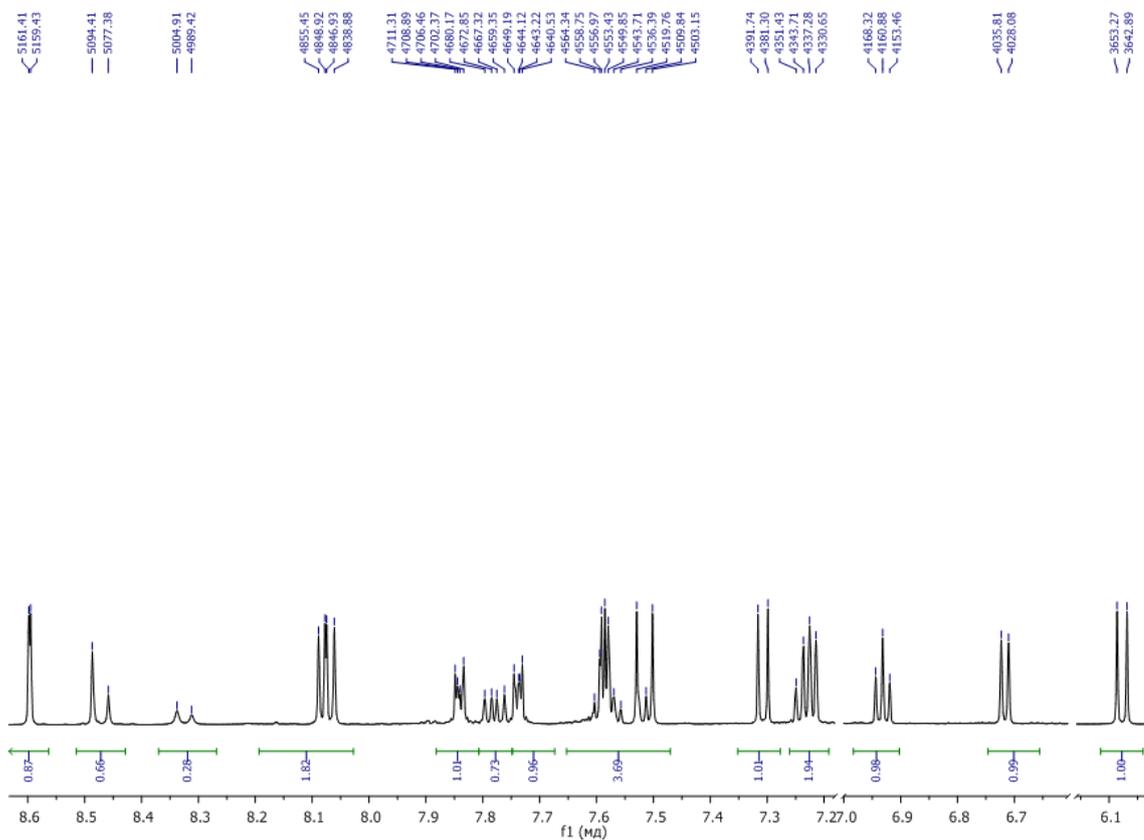


Figure S9. NMR ^1H spectrum of compound **2**, aromatic proton region

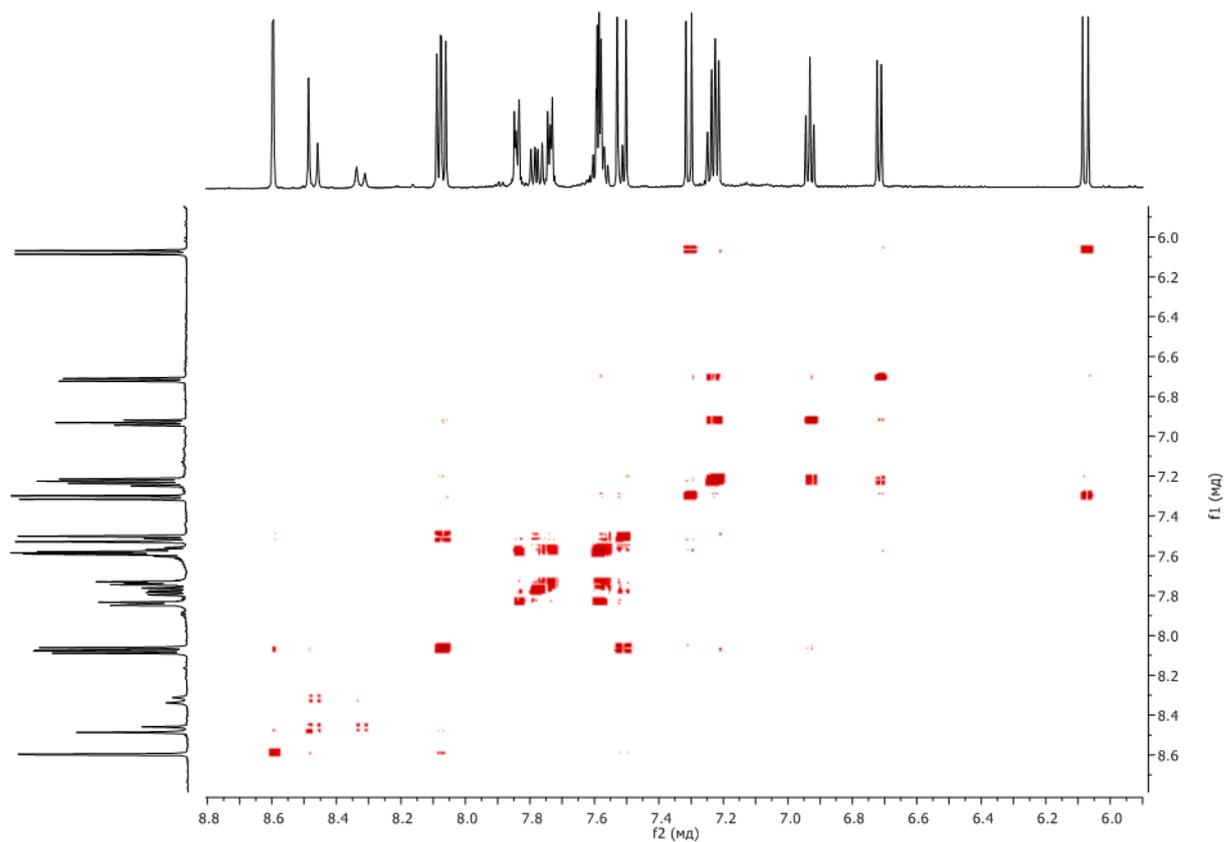


Figure S10. COSY ^1H - ^1H NMR spectrum of compound **2**, aromatic proton area

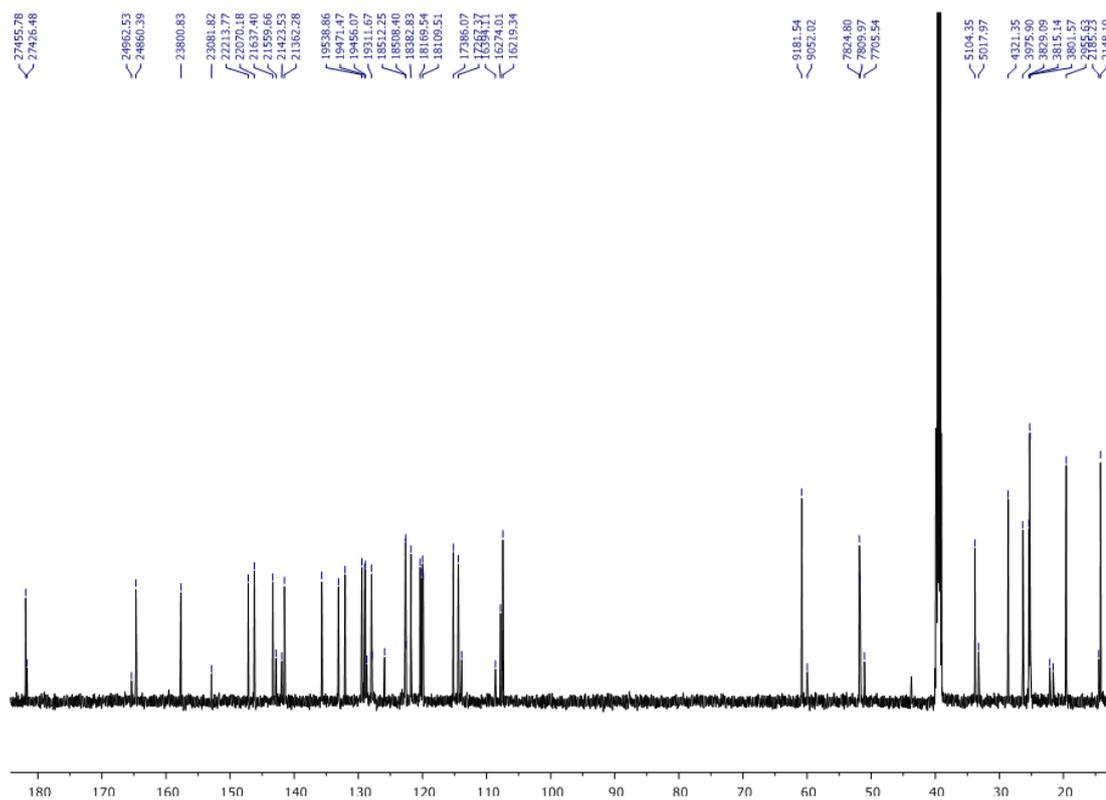


Figure S11. NMR ^{13}C spectrum of compound **2**

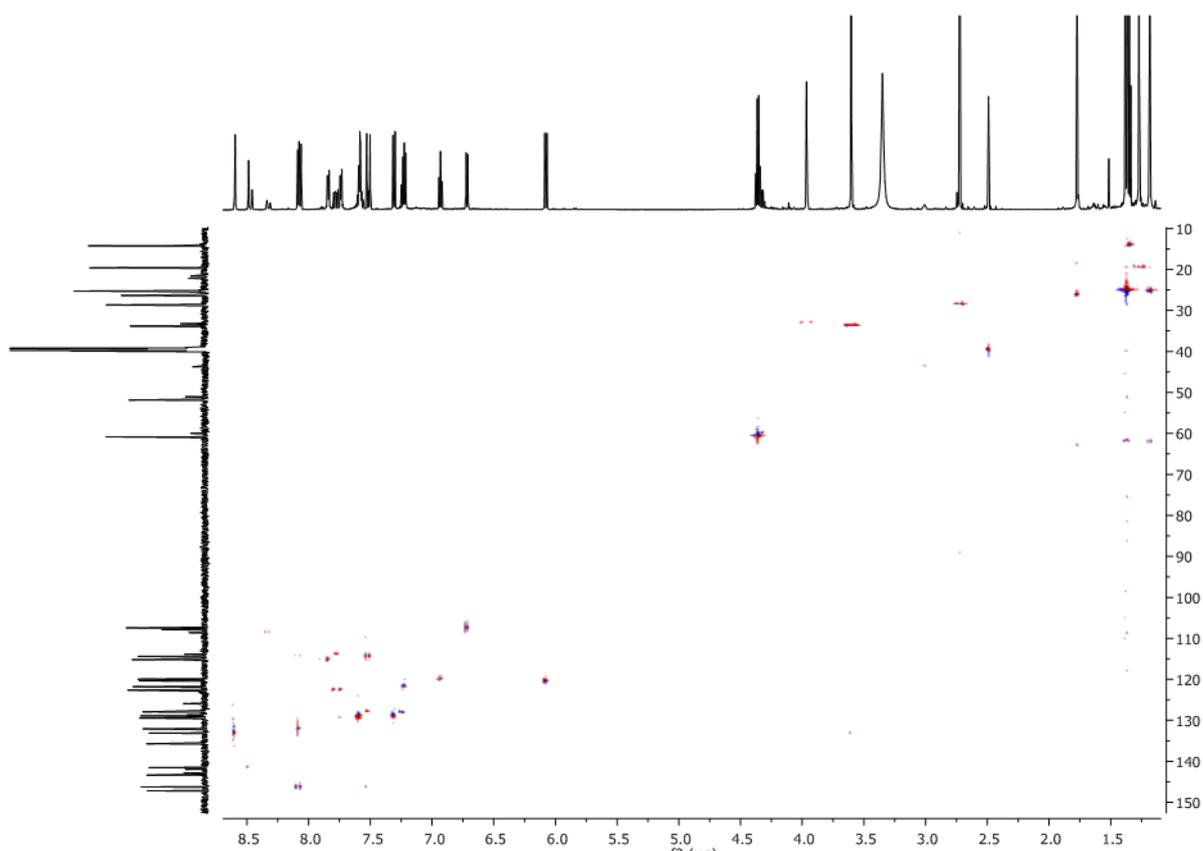


Figure S12. HSQC ^1H - ^{13}C NMR spectrum of compound **2**

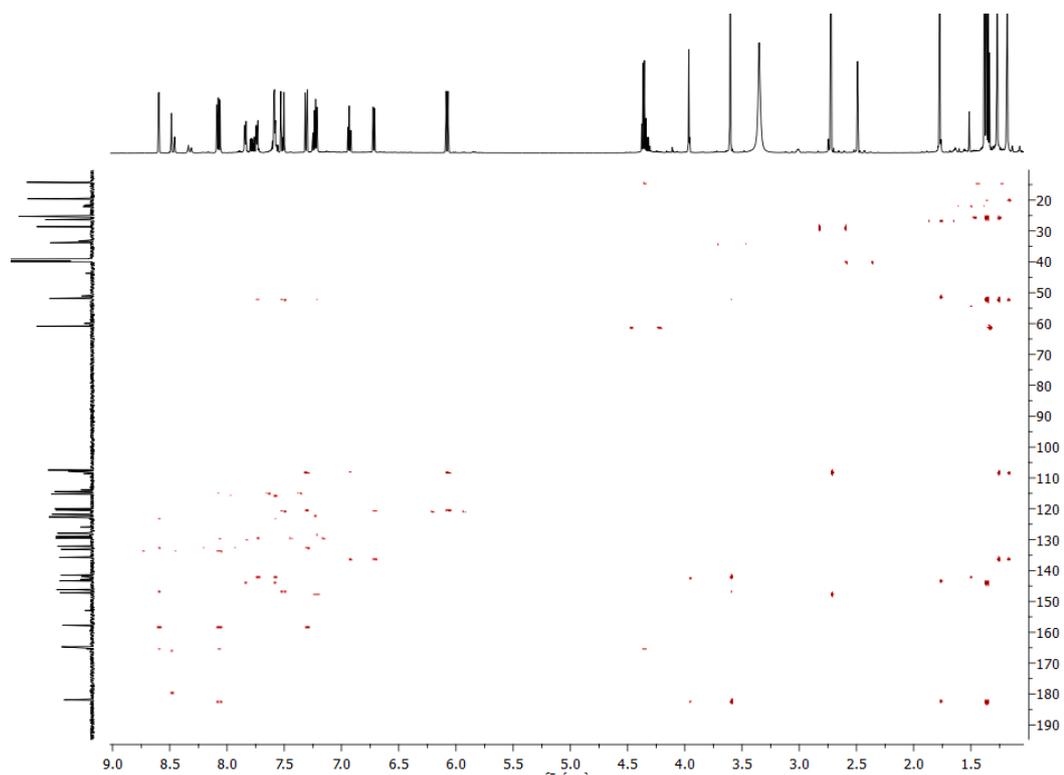


Figure S13. HMBC ^1H - ^{13}C NMR spectrum of compound 2

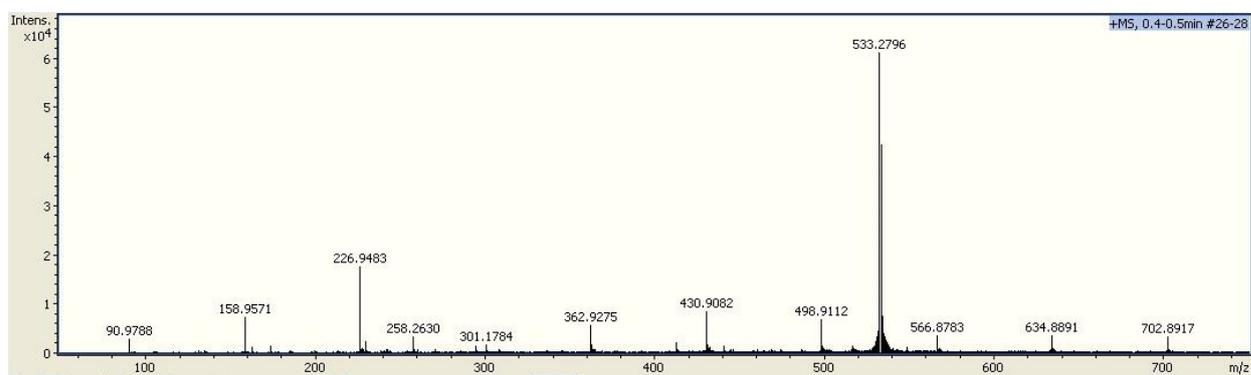


Figure S14. HRMS spectrum of compound 2

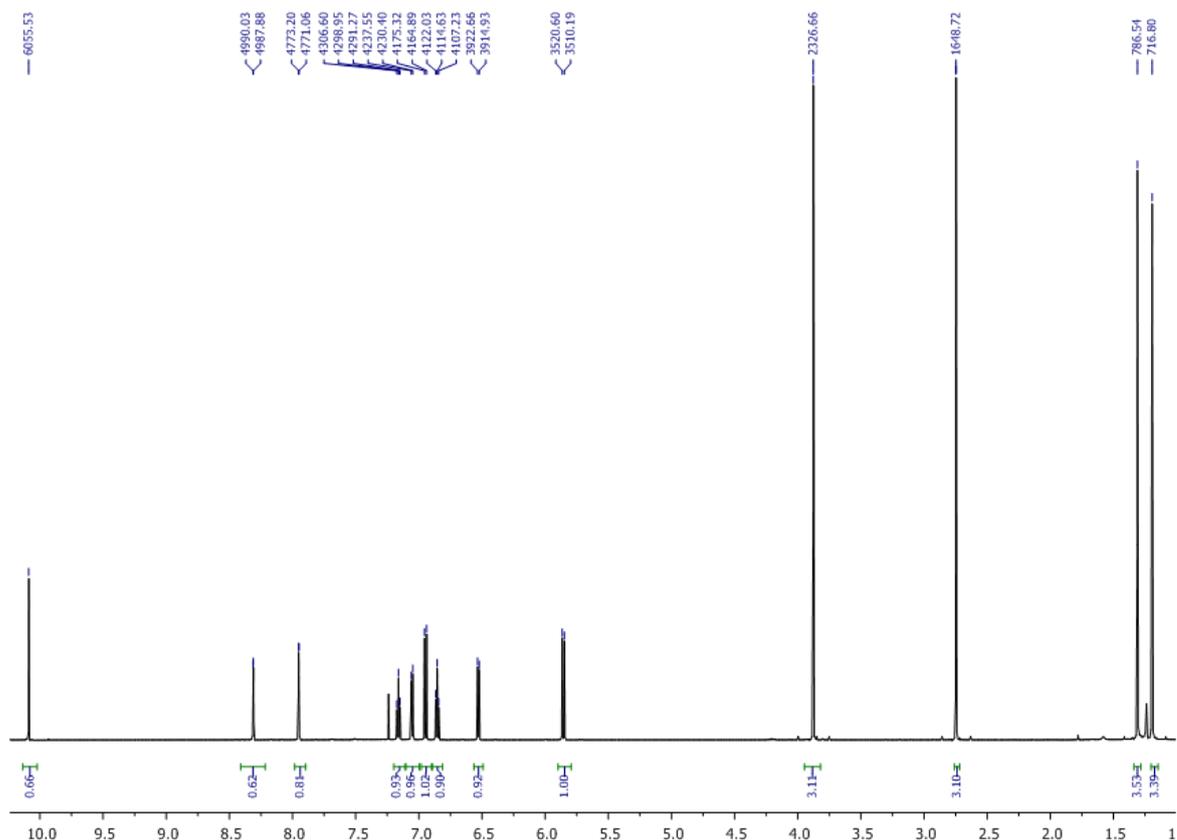


Figure S15. NMR ^1H spectrum of compound **3**, general view

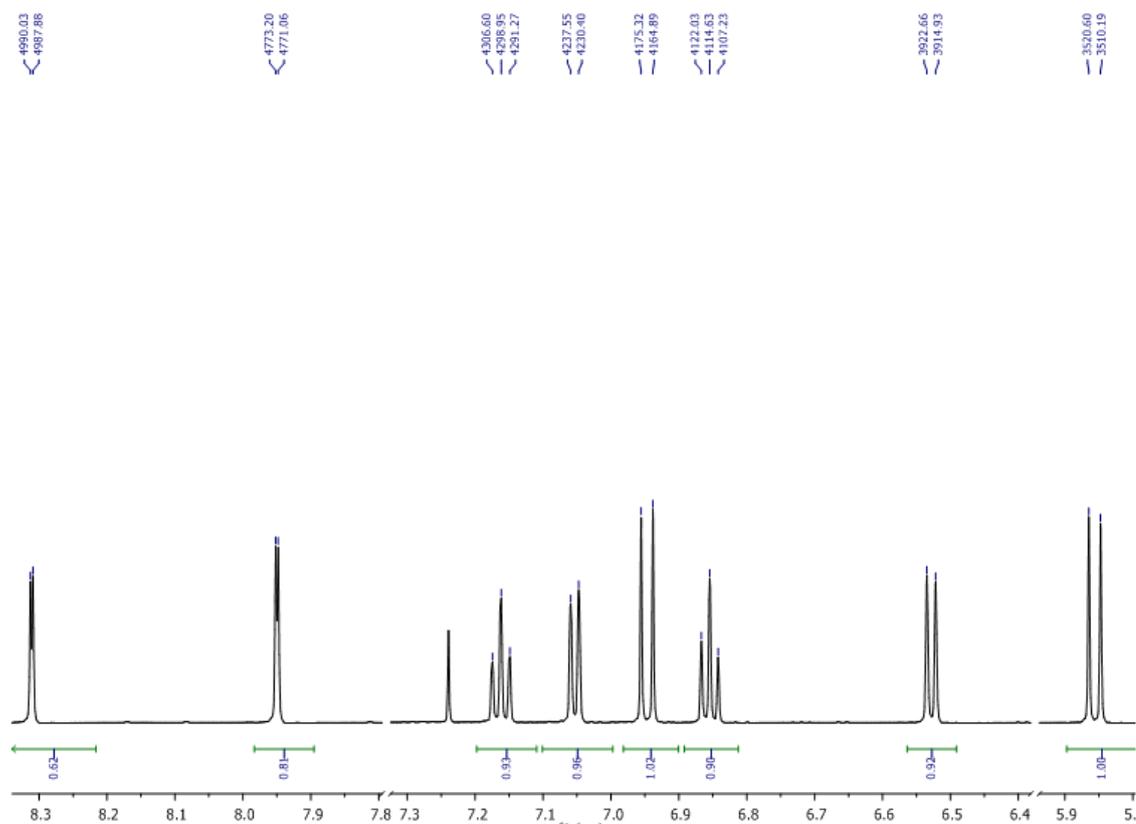


Figure S16. NMR ^1H spectrum of compound **3**, aromatic proton region

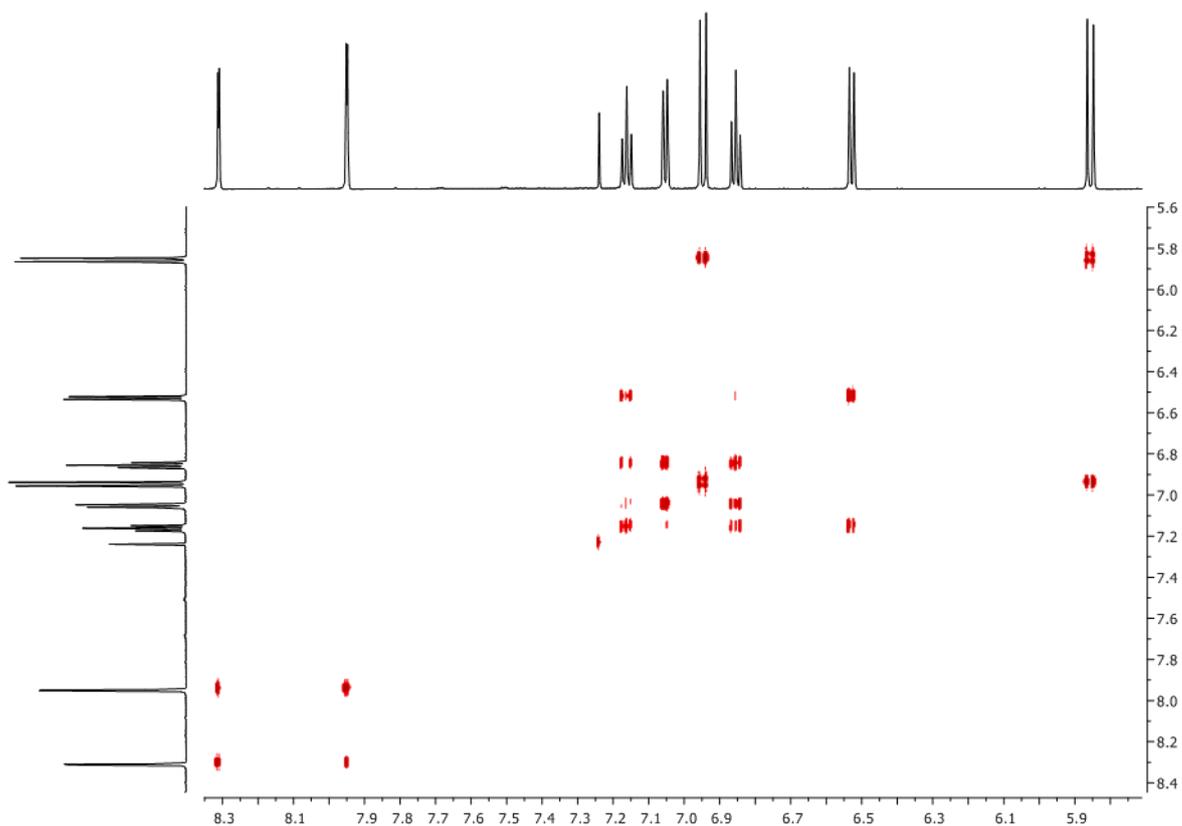


Figure S17. COSY ^1H - ^1H NMR spectrum of compound **3**, aromatic proton region

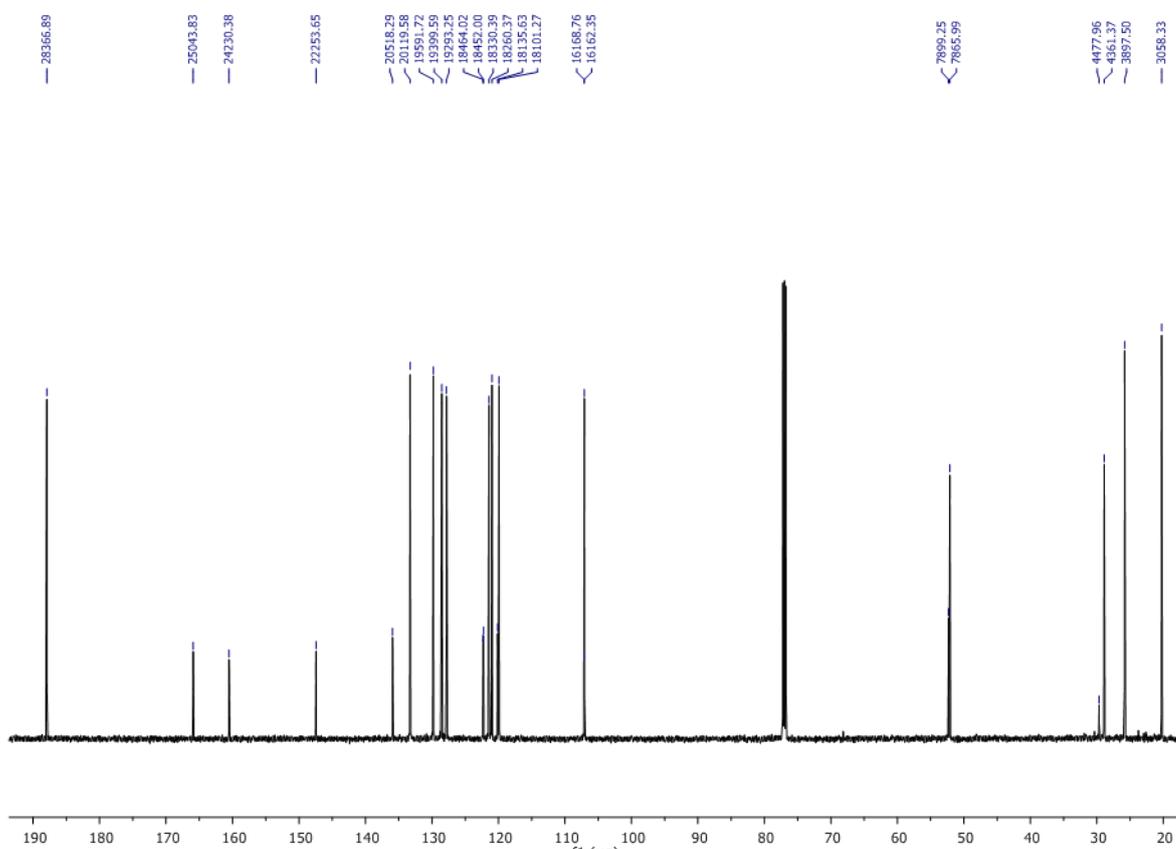


Figure S18. NMR ^{13}C spectrum of compound **3**, general view

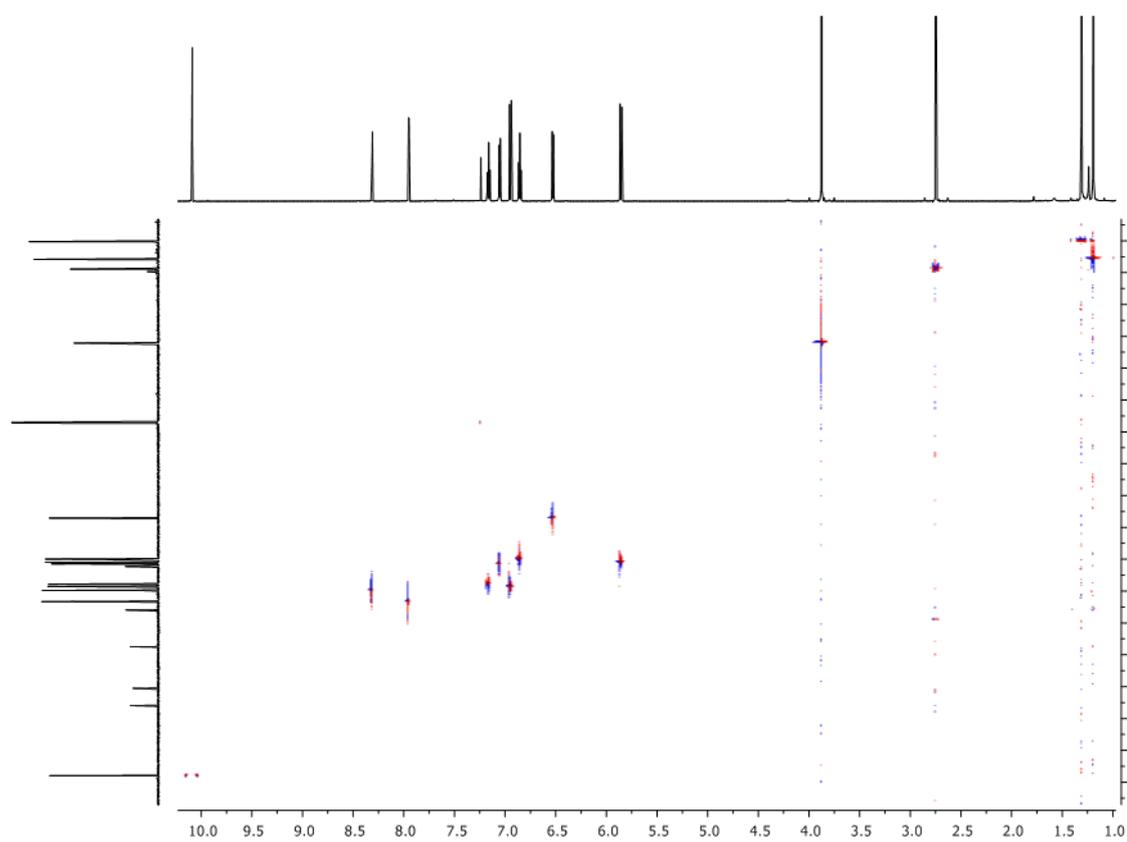


Figure S19. HSQC ^1H - ^{13}C NMR spectrum of compound **3**

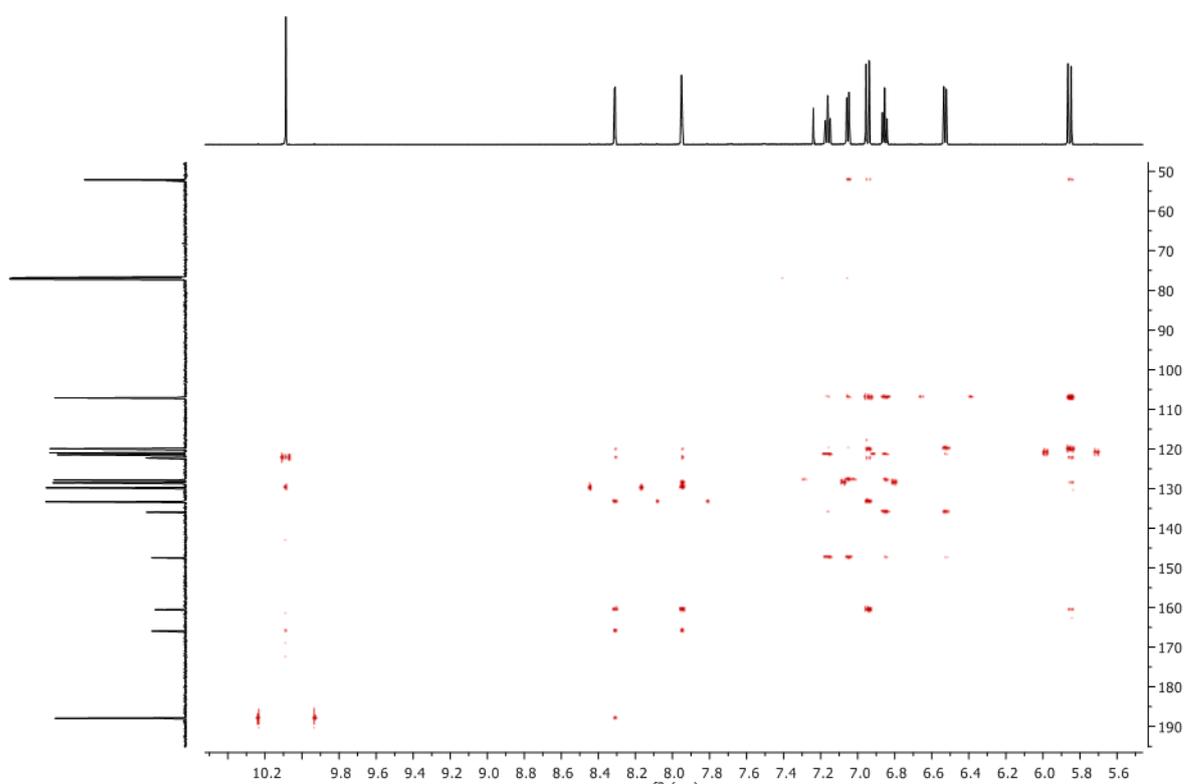


Figure S20. HMBC ^1H - ^{13}C NMR spectrum of compound **3**, aromatic proton correlations

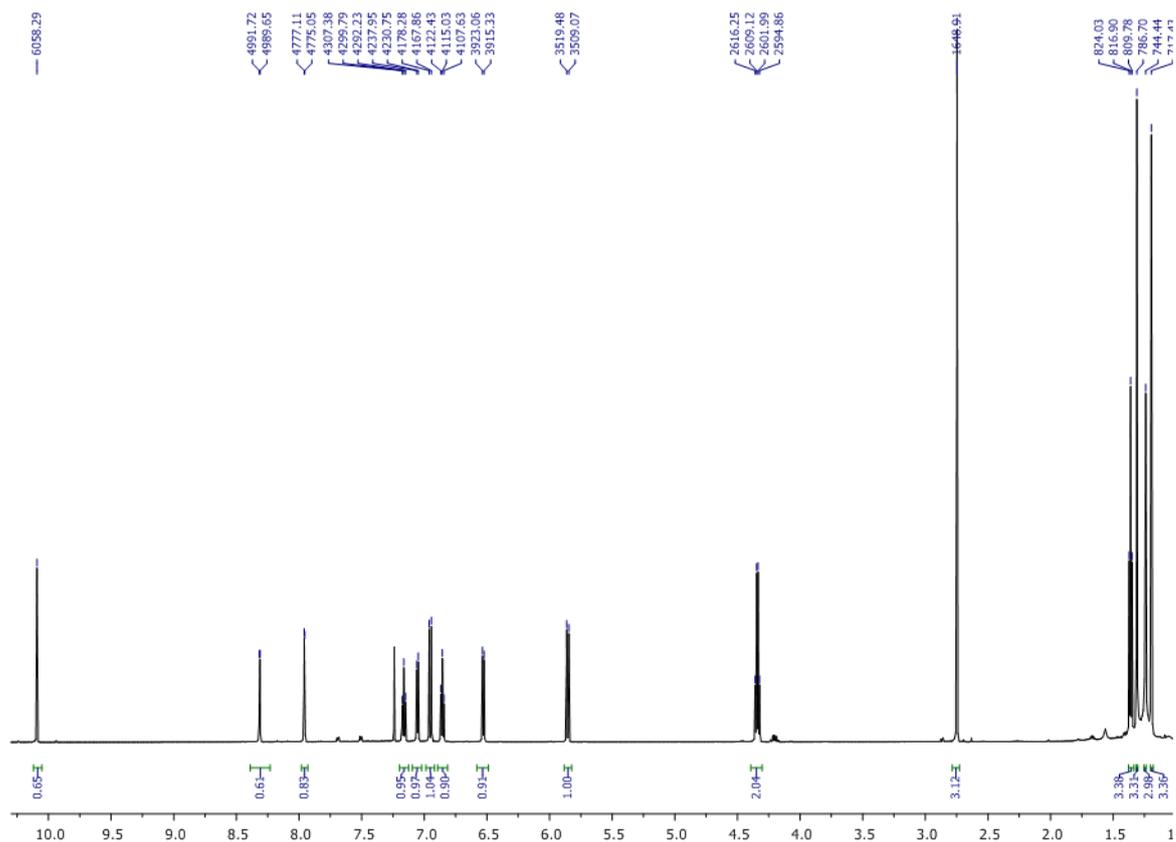


Figure S21. NMR ^1H spectrum of compound **4**, general view

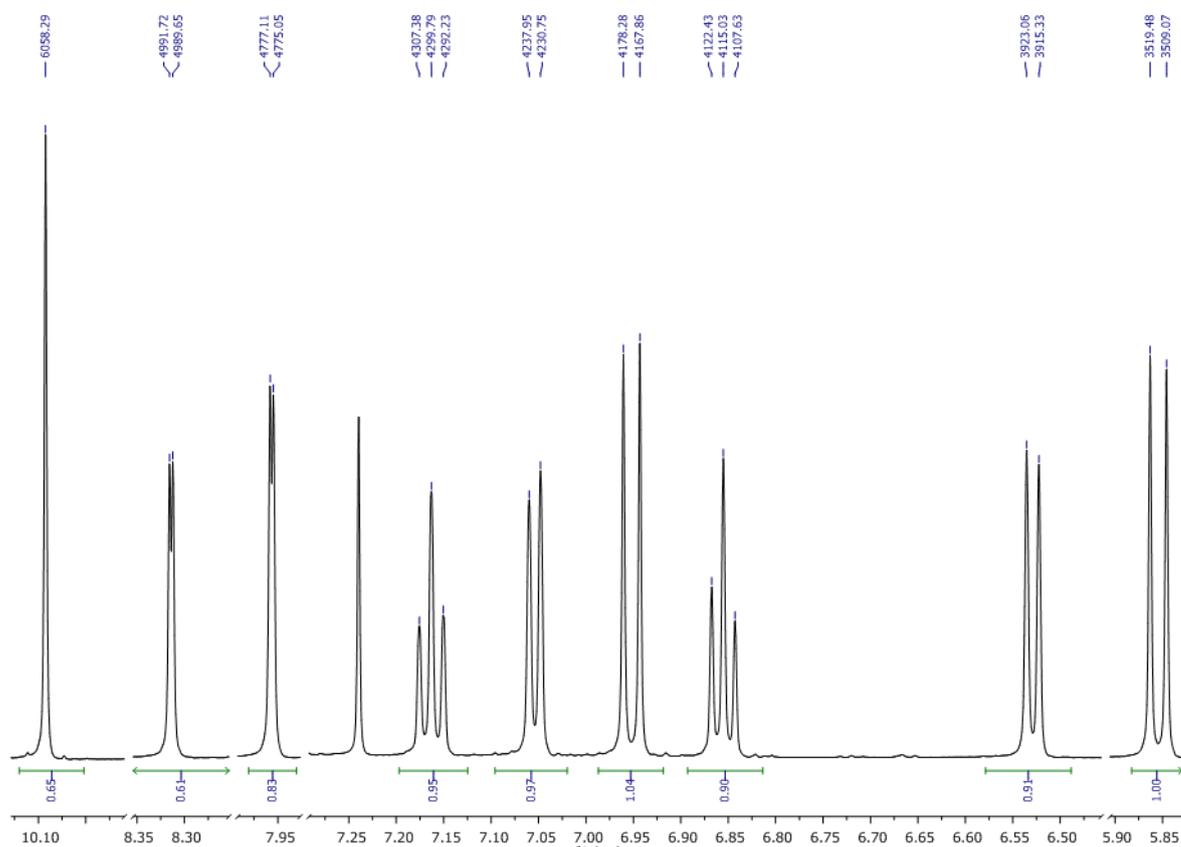


Figure S22. NMR ^1H spectrum of compound **4**, aromatic proton region

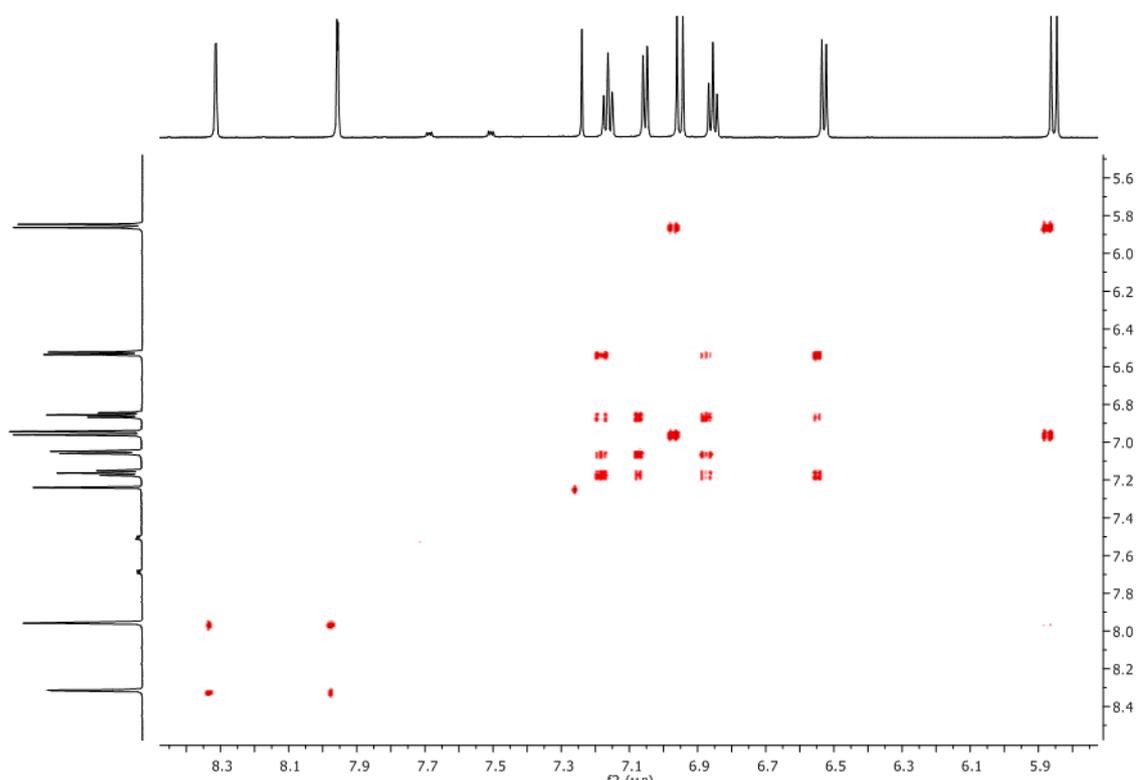


Figure S23. COSY ^1H - ^1H NMR spectrum of compound **4**, aromatic proton region

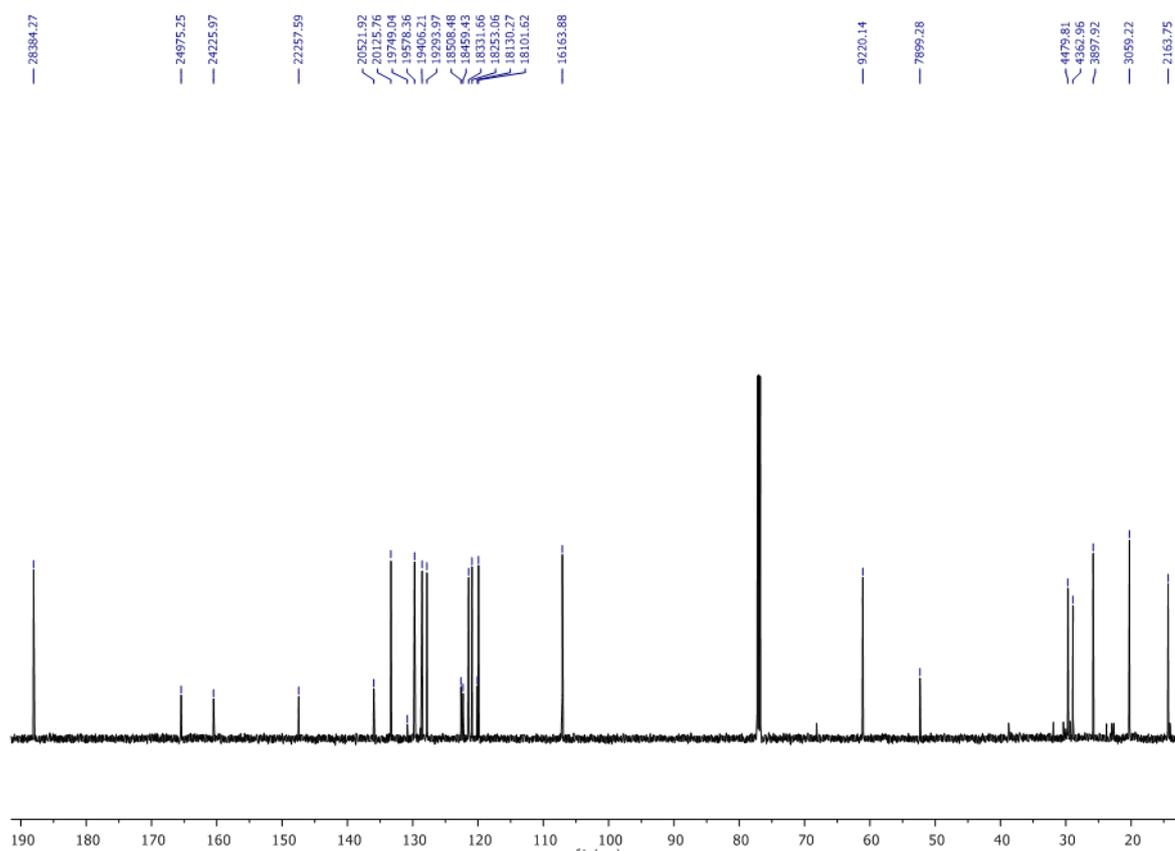


Figure S24. NMR ^{13}C spectrum of compound **4**

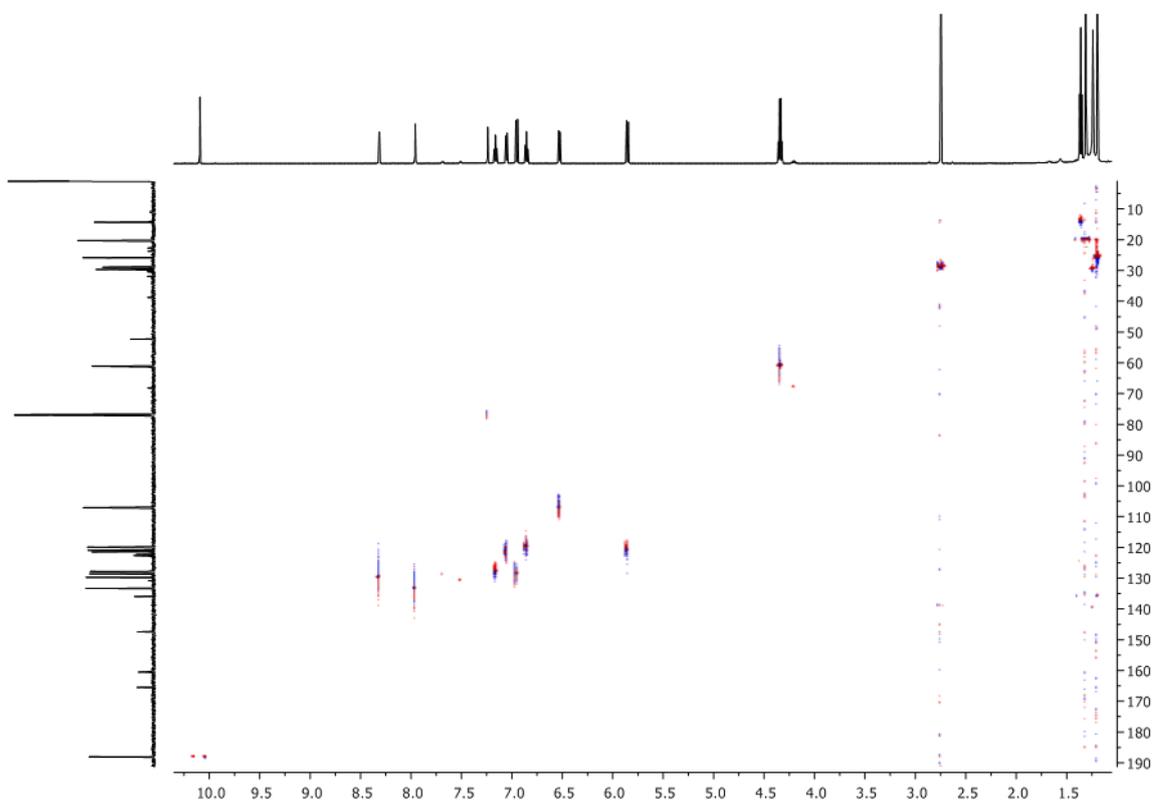


Figure S25. HSQC ^1H - ^{13}C NMR spectrum of compound **4**

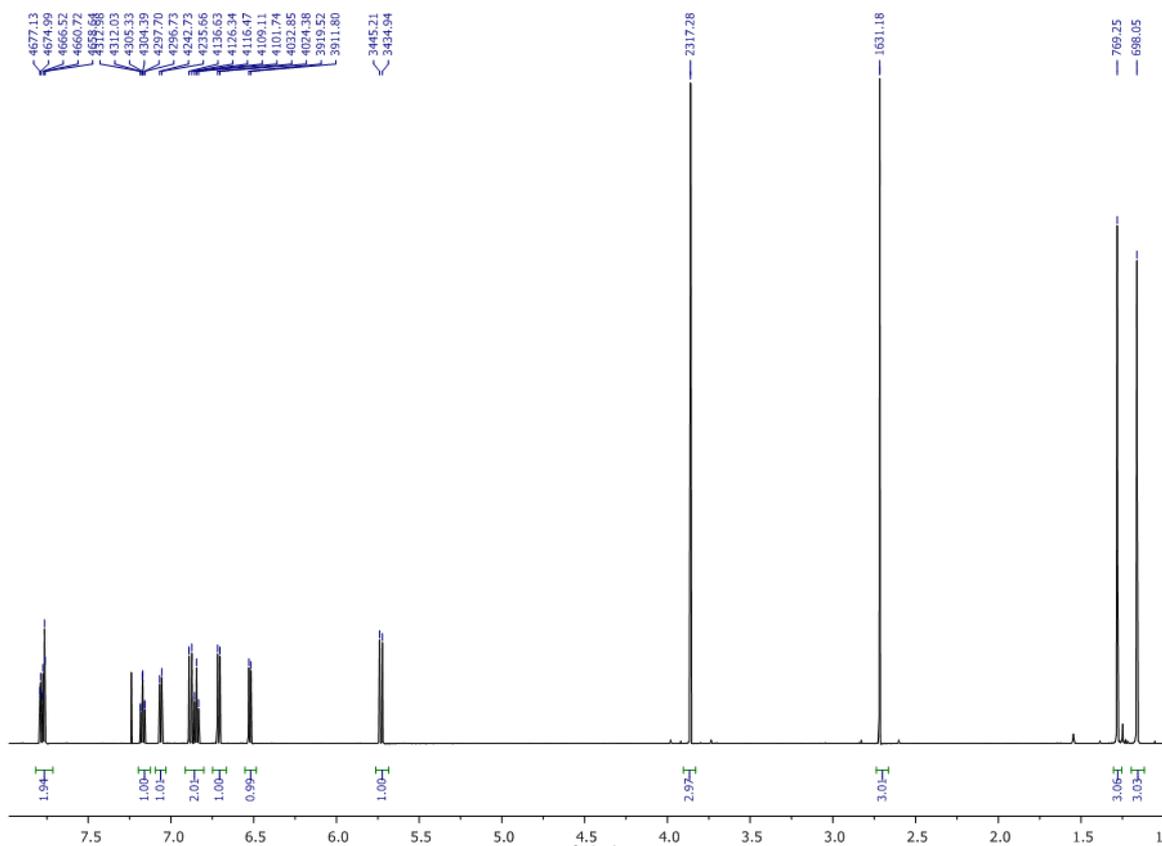


Figure S26. NMR ^1H spectrum of compound **5**, general view

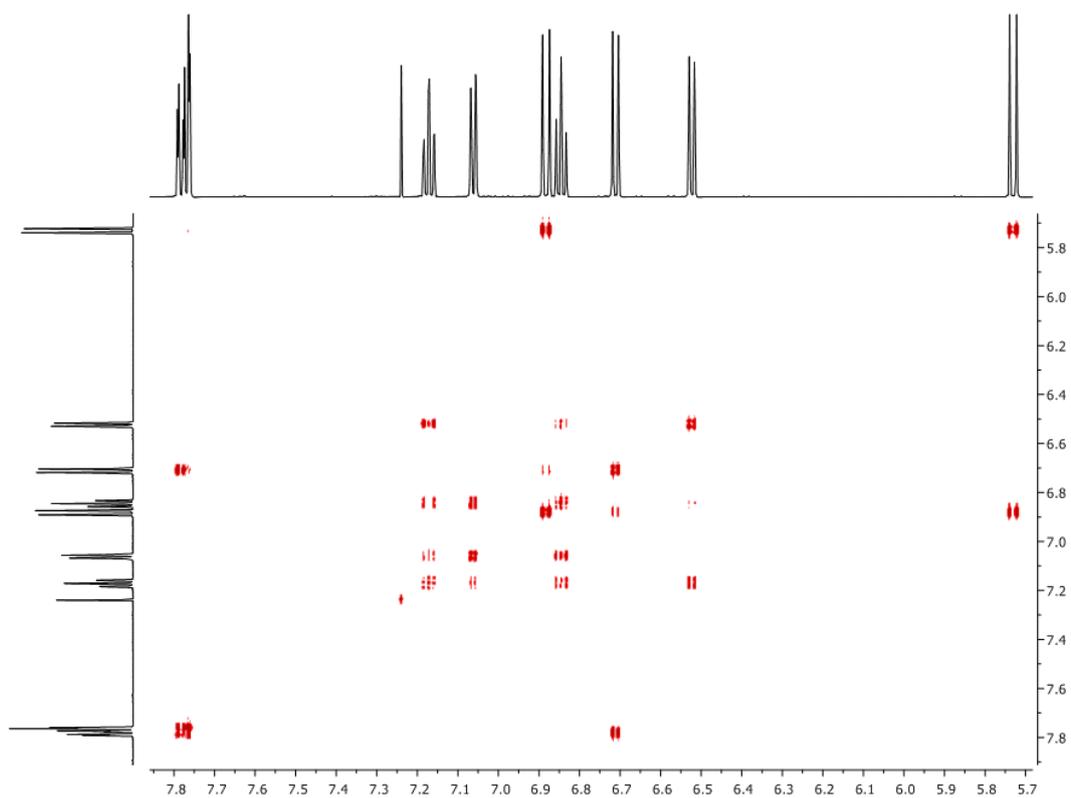


Figure S27. COSY ¹H-¹H NMR spectrum of compound **5**, aromatic proton region

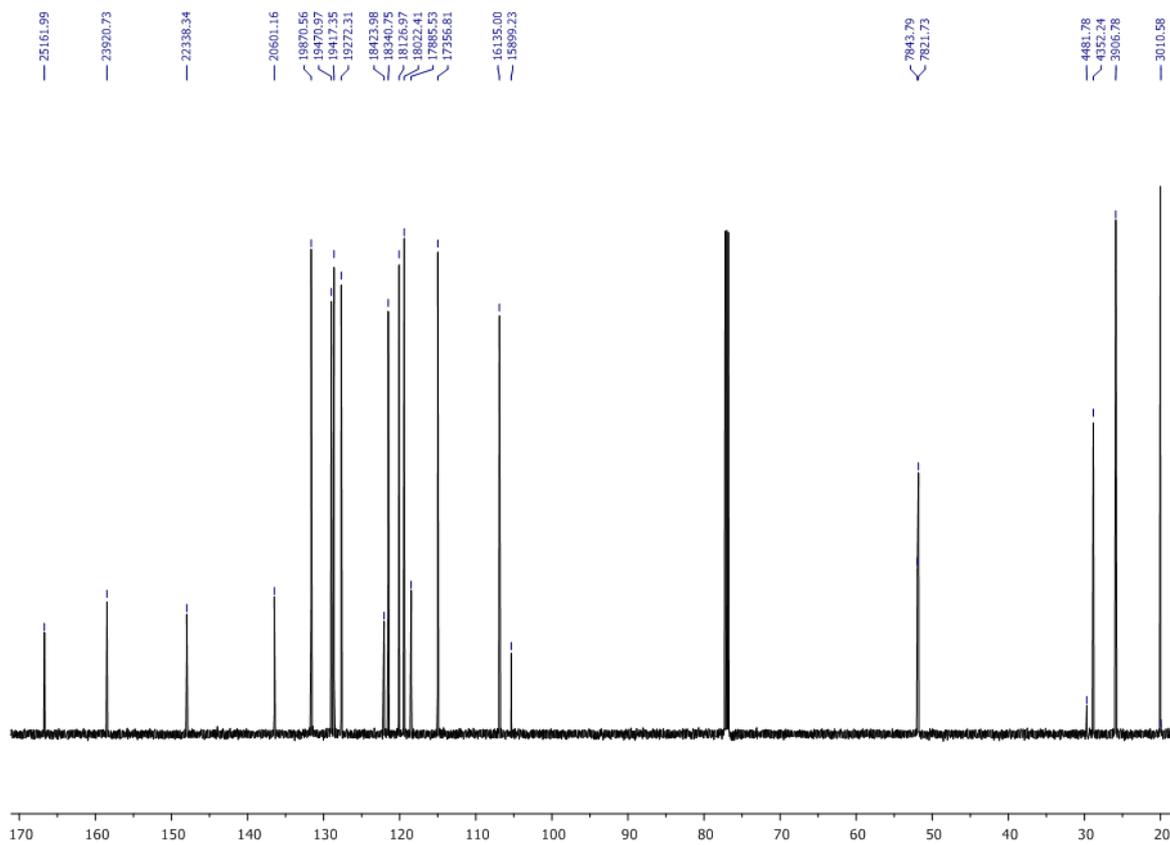


Figure S28. NMR ¹³C spectrum of compound **5**

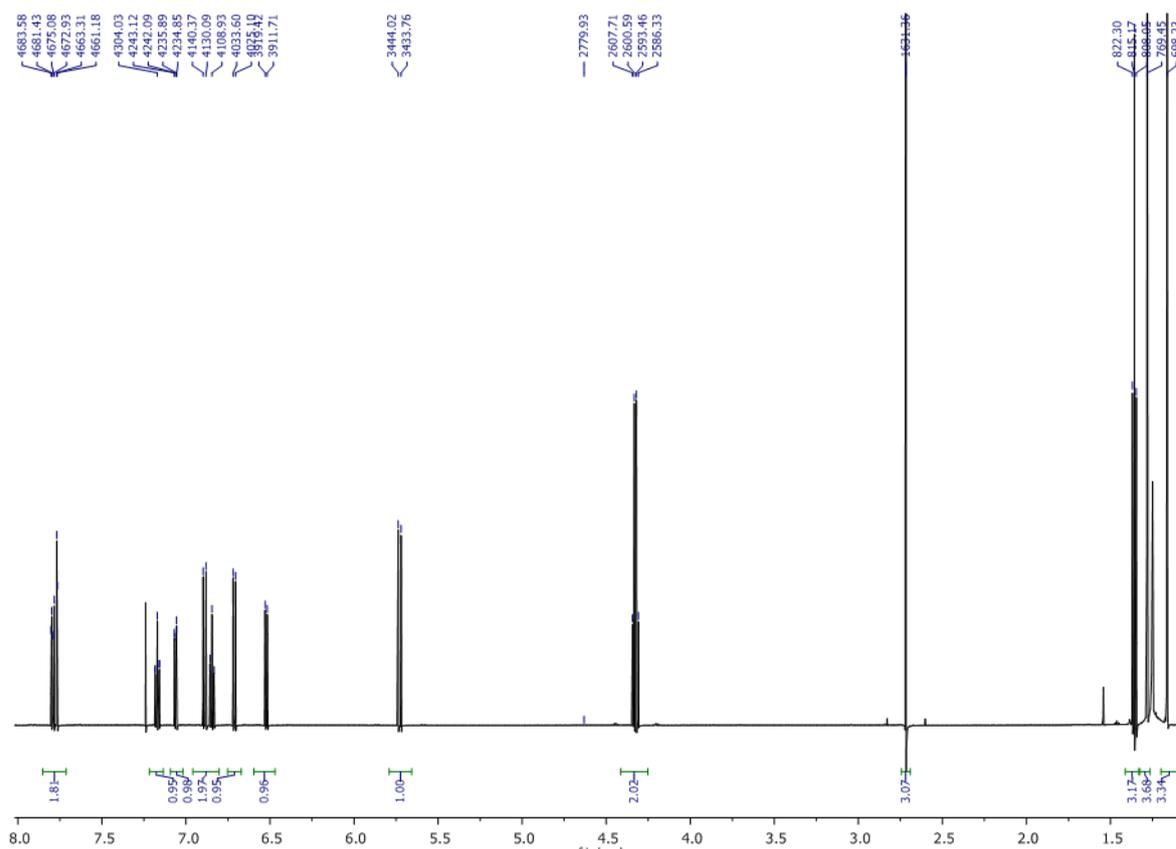


Figure S29. ^1H NMR spectrum of compound **6**

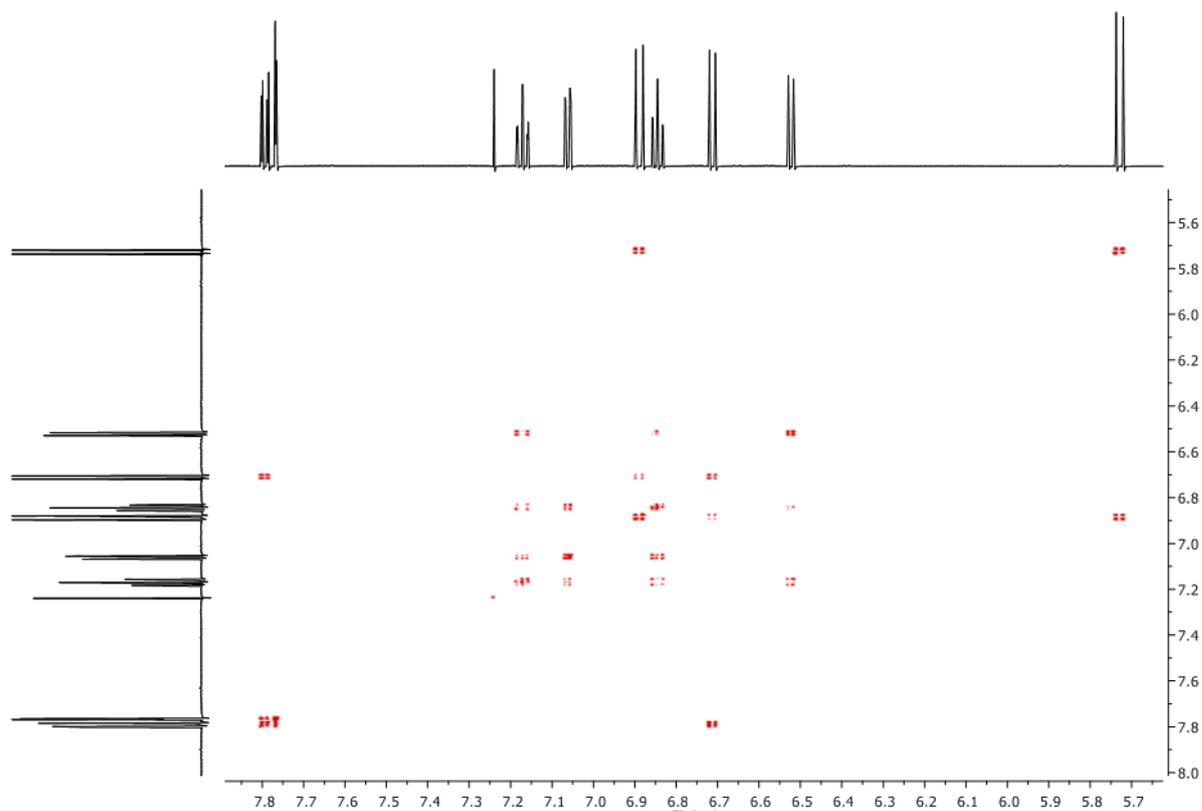


Figure S30. COSY ^1H - ^1H NMR spectrum of compound **6**, aromatic proton region

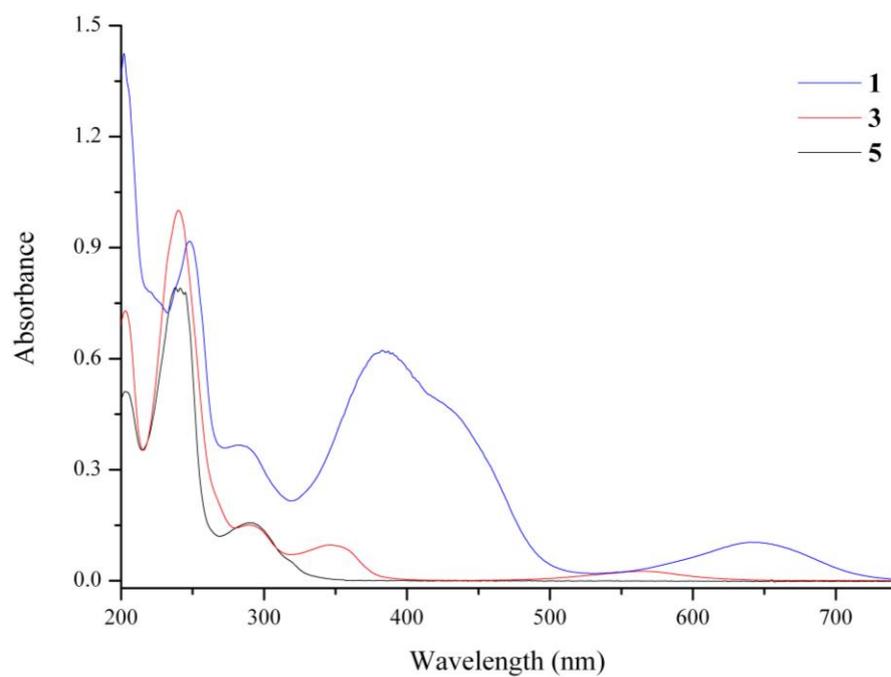


Figure S31. Electronic absorption spectra of compounds **1**, **3** and **5** in acetonitrile before irradiation, $C = 2 \cdot 10^{-5} \text{ M}$, $T = 293 \text{ K}$.

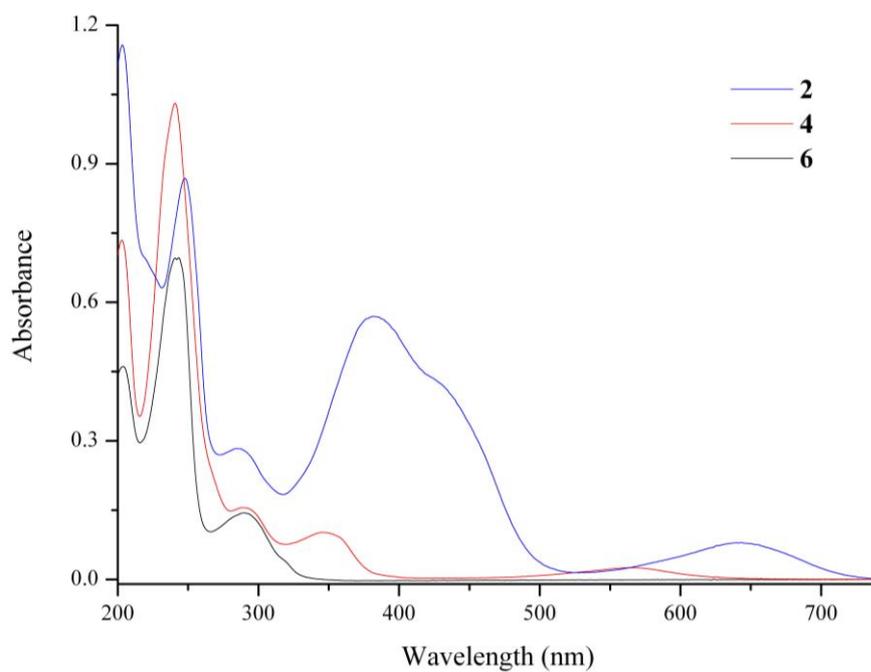


Figure S32. Electronic absorption spectra of compounds **2**, **4** and **6** in acetonitrile before irradiation, $C = 2 \cdot 10^{-5} \text{ M}$, $T = 293 \text{ K}$.

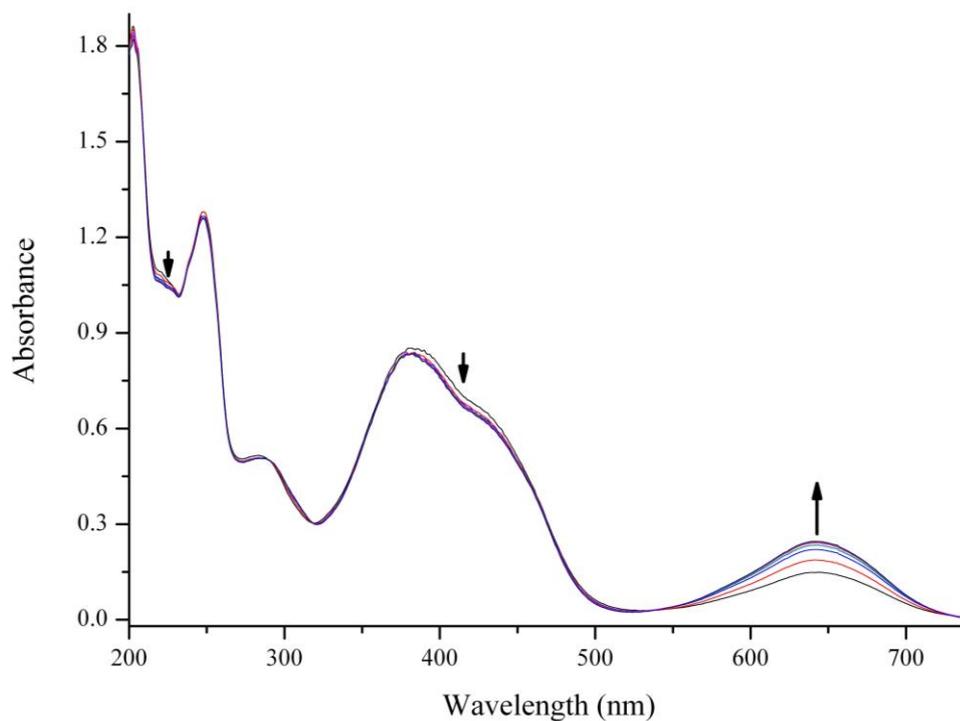


Figure S33. Absorption spectra changes of **1** under UV irradiation ($\lambda_{\text{irr}} = 365 \text{ nm}$) in acetonitrile, $C = 3.7 \cdot 10^{-5} \text{ M}$, $T = 293 \text{ K}$.

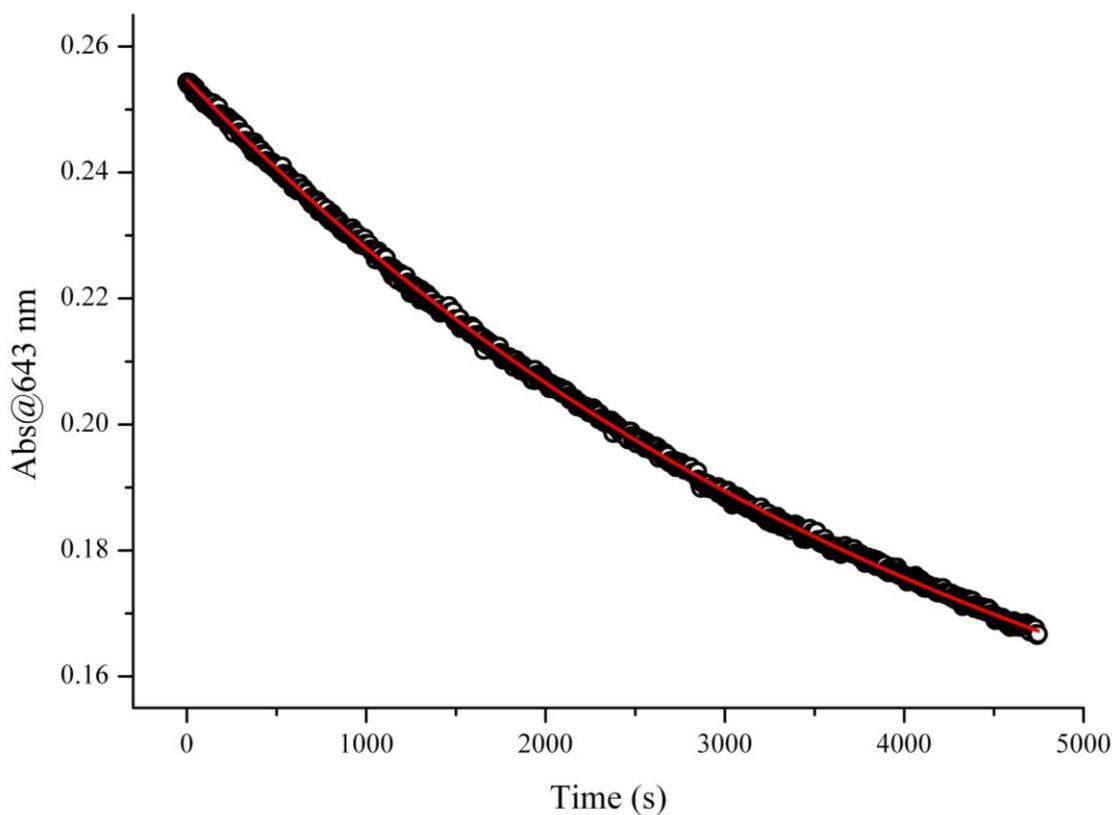


Figure S34. Kinetic curve of thermal recyclization of compound **1** in MeCN at 293 K. Circle – experimental data, red line – the approximation by monoexponential function

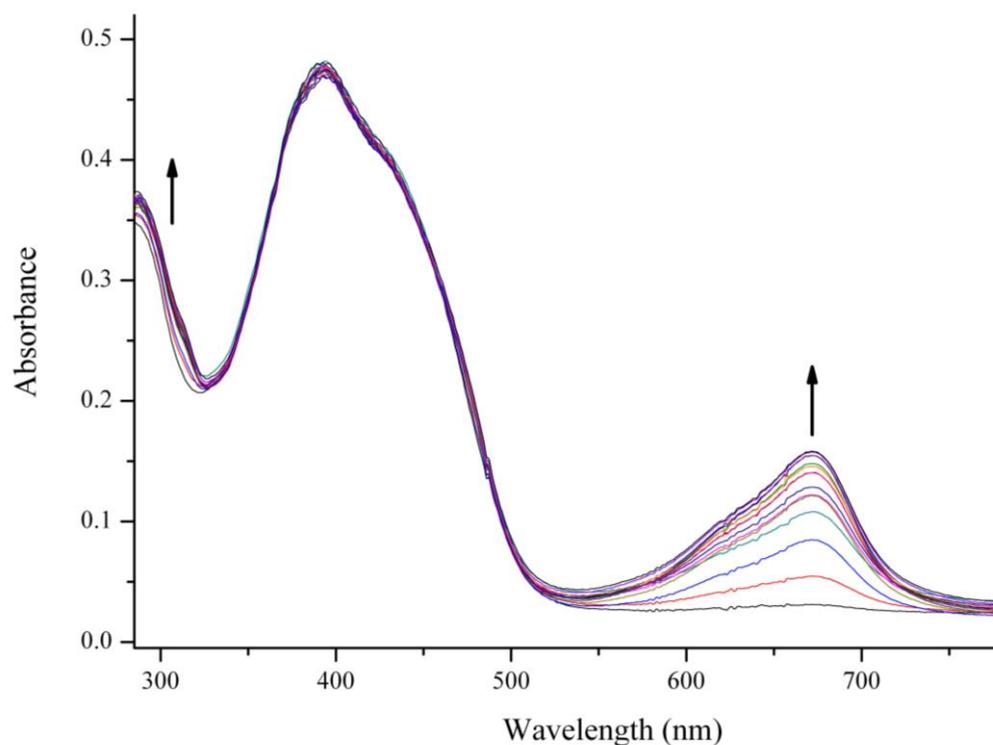


Figure S35. Absorption spectra changes of **1** under UV irradiation ($\lambda_{\text{irr}} = 365 \text{ nm}$) in toluene, $T = 293 \text{ K}$.

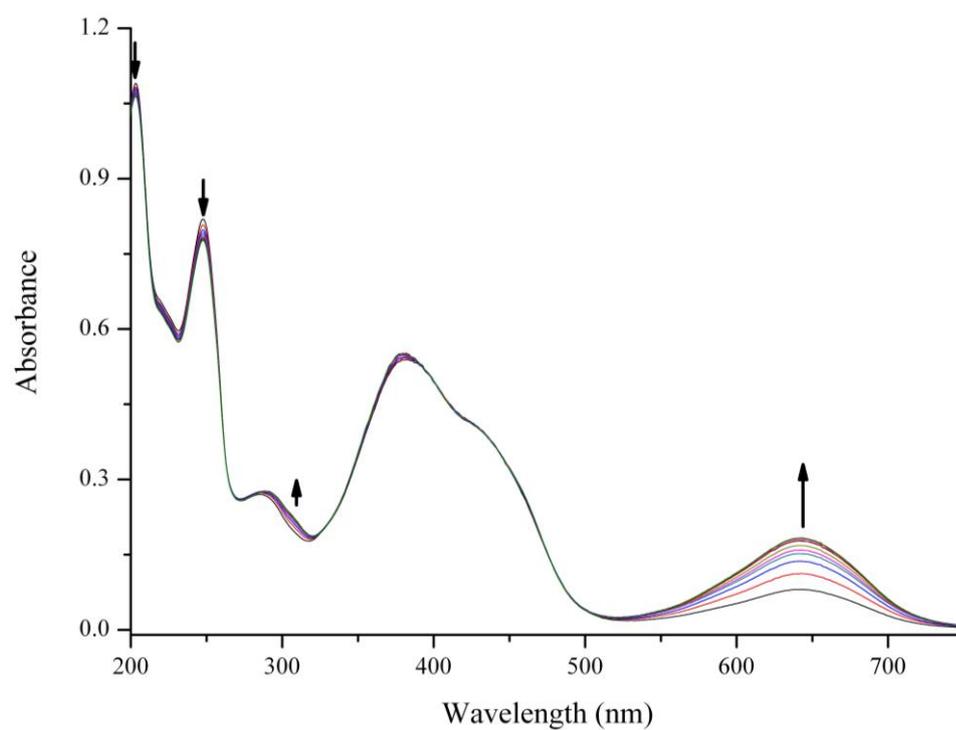


Figure S36. Absorption spectra changes of **2** under UV irradiation ($\lambda_{\text{irr}} = 365 \text{ nm}$) in acetonitrile, $C = 3.7 \cdot 10^{-5} \text{ M}$, $T = 293 \text{ K}$.

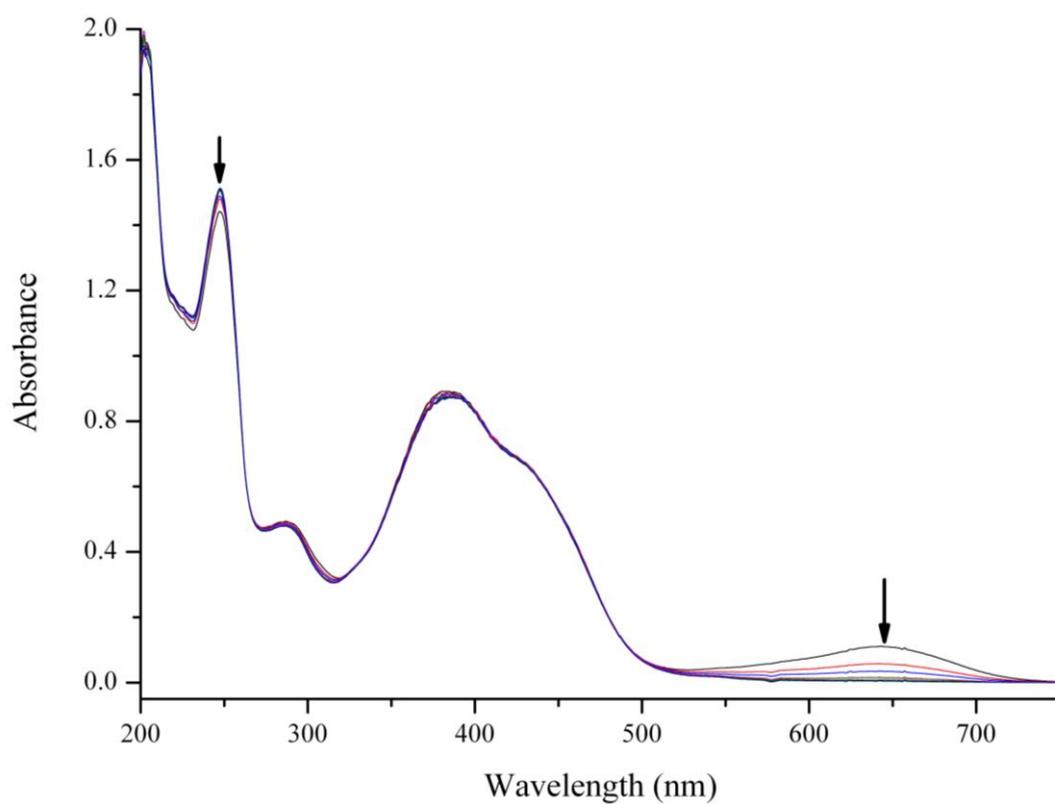


Figure S37. Absorption spectra changes of **2** under visible light irradiation ($\lambda_{\text{irr}} = 578 \text{ nm}$) in acetonitrile, $C = 4 \cdot 10^{-5} \text{ M}$, $T = 293 \text{ K}$.

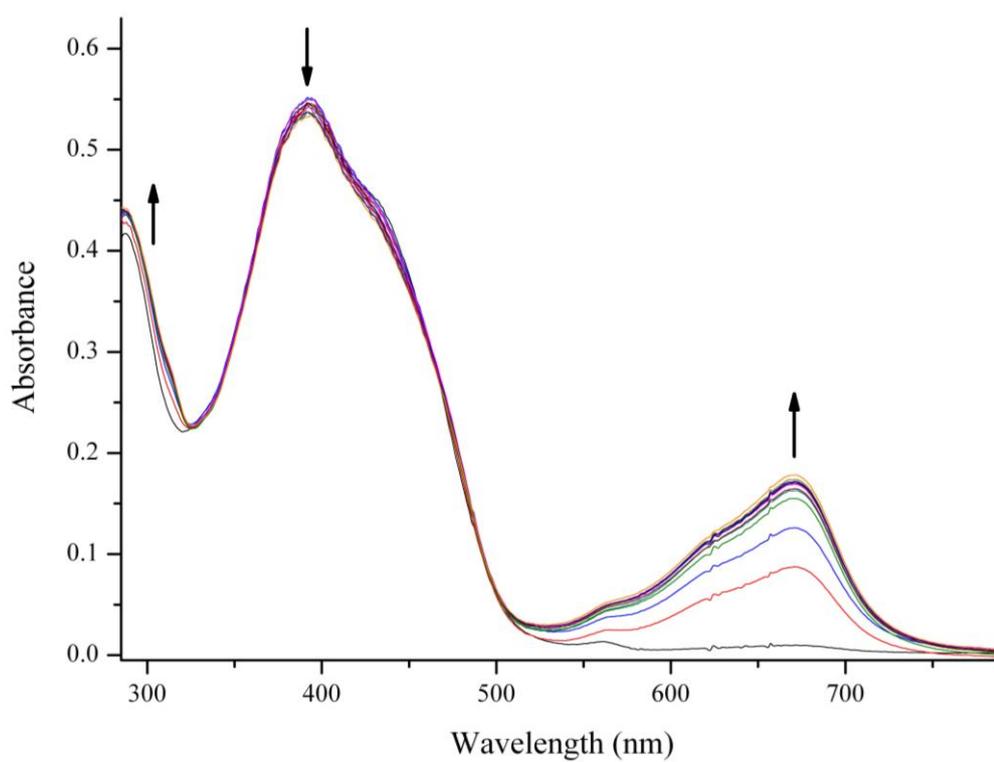


Figure S38. Absorption spectra changes of **2** under UV irradiation ($\lambda_{\text{irr}} = 365 \text{ nm}$) in toluene, $T = 293 \text{ K}$.

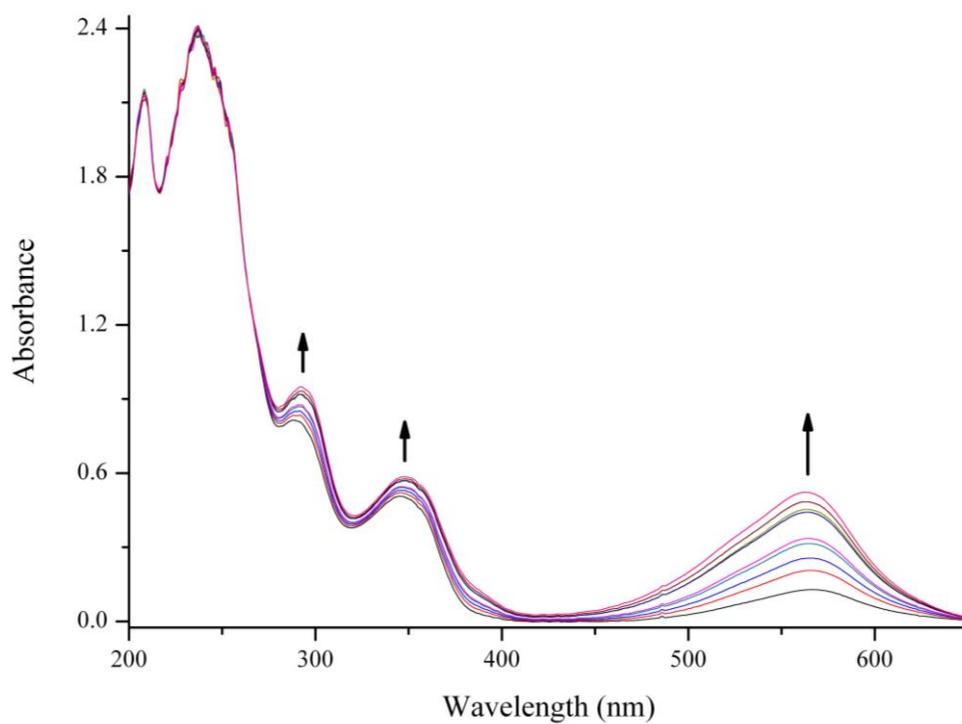


Figure S39. Absorption spectra changes of **3** under UV irradiation ($\lambda_{\text{irr}} = 365 \text{ nm}$) in acetonitrile, $C = 1.08 \cdot 10^{-4} \text{ M}$, $dt = 1 \text{ s}$, $T = 293 \text{ K}$.

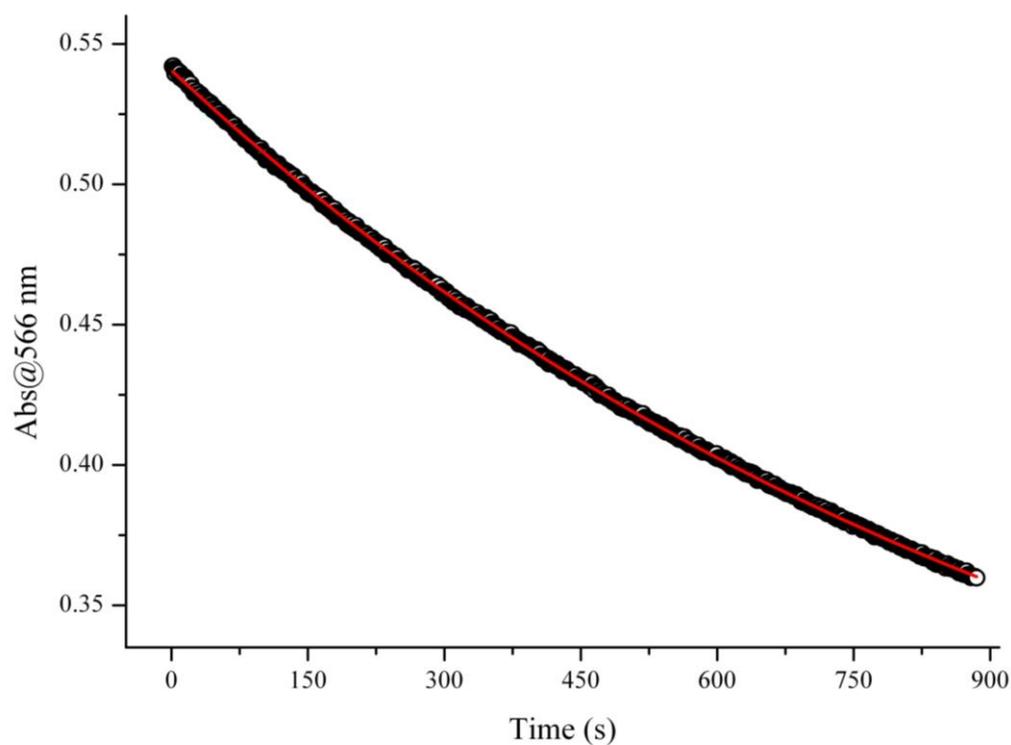


Figure S40 Kinetic curve for thermal recyclization of compound **3** in acetonitrile, $T = 293 \text{ K}$. Circle – experimental data, red line – approximation by monoexponential function.

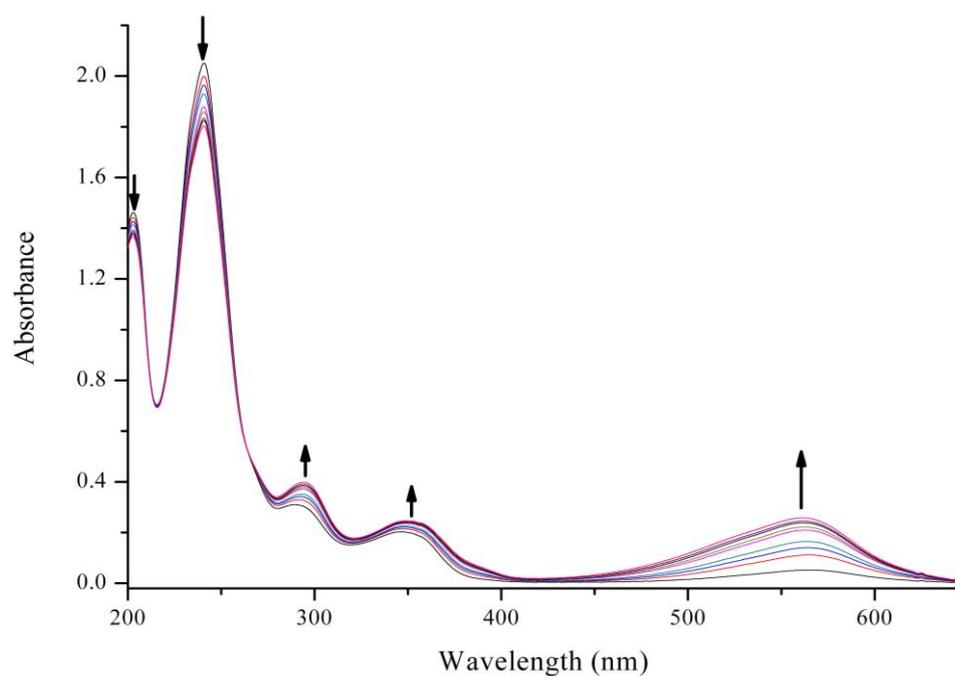


Figure S41. Absorption spectra changes of **4** under UV irradiation ($\lambda_{\text{irr}} = 365$ nm) in acetonitrile, $C = 3.98 \cdot 10^{-5}$ M, $dt = 5$ s, $T = 293$ K.

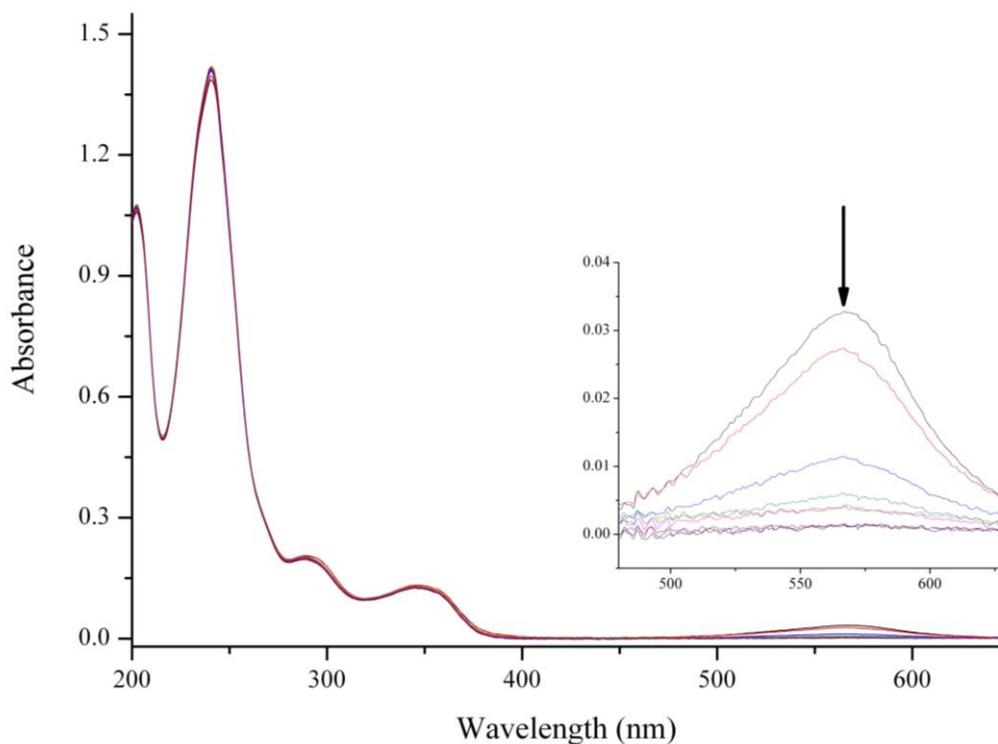


Figure S42. Absorption spectra changes of **4** under visible light irradiation ($\lambda_{\text{irr}} = 578$ nm) in acetonitrile, $C = 4 \cdot 10^{-5}$ M, $T = 293$ K.

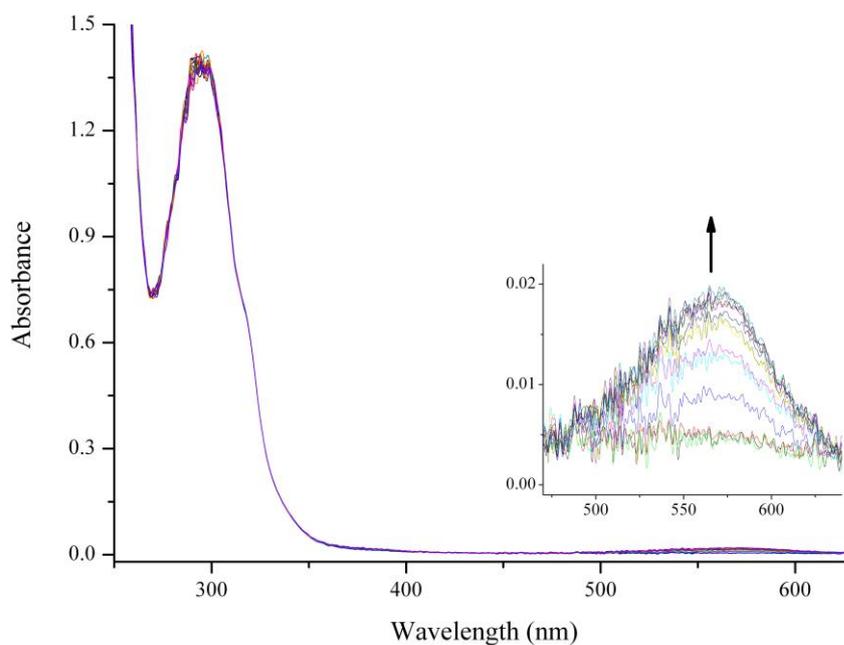


Figure S43. Absorption spectra changes of **5** under UV irradiation ($\lambda_{\text{irr}} = 365 \text{ nm}$) in acetonitrile, $C = 2.41 \cdot 10^{-4} \text{ M}$, $\text{dt} = 5 \text{ s}$, $T = 293 \text{ K}$.

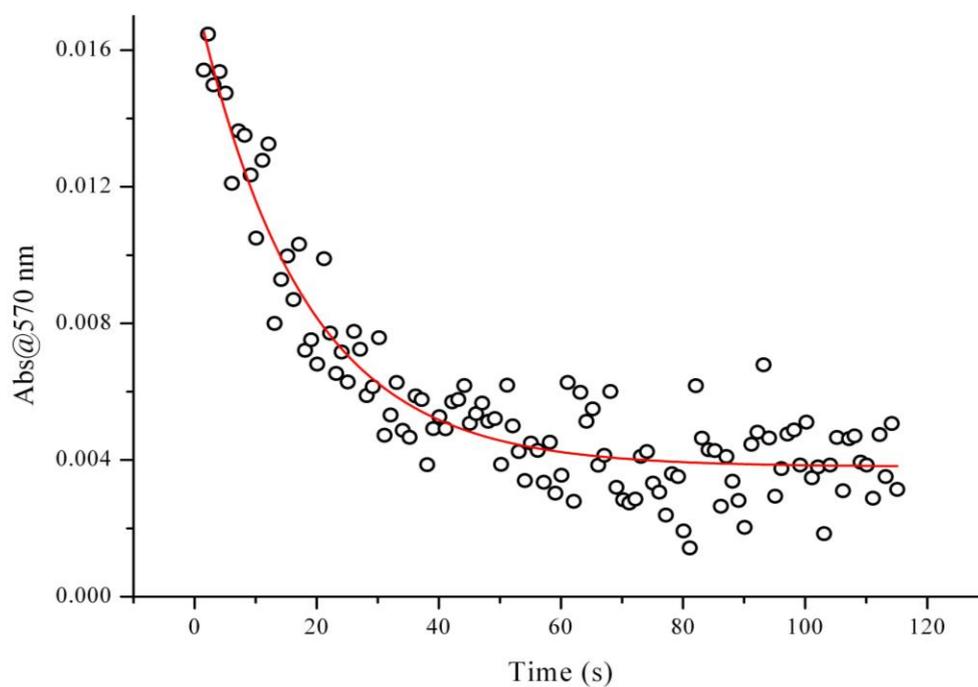


Figure S44. Kinetic curve for thermal recyclization of compound **5** in acetonitrile, $T = 293 \text{ K}$. Circle – experimental data, red line – the approximation by monoexponential function.