Supplementary Information of "Synthesis and photochromic properties of oxime derivatives of 2,3-diarylcyclopent-2-en-1-ones"

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Methods and reagents

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer. Mass spectra were obtained on a Kratos mass spectrometer (70 eV) with direct sample injection into the ion source. Melting points were measured on a Boetius hot stage and were not corrected. IR spectra were obtained on a Specord M80 or M82 spectrometer in KBr pellets. High resolution mass spectra were obtained on a Bruker maXis spectrometer. Microanalyses were obtained using a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer.

Commercially available reagents and solvents were used. DCPs **1** have been prepared by the previously reported method [1]. Column chromatography was performed using silica gel 60 (70–230 mesh); TLC analysis was conducted on silica gel 60 F_{254} plates.

Electronic absorption spectra were recorded on a LOMO SF-56 spectrophotometer. The experiments were performed in acetonitrile (Acros) solutions ($C = 2 \cdot 10^{-5}$ mol·L^{-1}) at 293 K in the air presence. Photocoloration was carried out using 6W Vilber Lourmat (France) UV-lamp model VL-6.LC (365 nm light). Quantum yields of ring-closure ($\varphi_{A\rightarrow B}$) and ring-opening ($\varphi_{A\rightarrow B}$) processes were calculated by early reported techniques [1-3]. For fatigue resistance

determination the samples were alternatively irradiated with UV- and visible light (to reach photostationary state). It was performed no more than 20 cycles; higher values of fatigue resistance were calculated by extrapolation of experimental data.

Experimental techniques and spectral data of oxime derivatives 2-6

Monooximes 2 (general method). The mixture of DCP **1** (2.0 mmol), hydroxylamine hydrochloride (6.0 mmol) and anhydrous sodium acetate (6.0 mmol) in ethanol (7 mL) was refluxed for 3 h and poured into crushed ice (70 mL). The residue was filtered off, washed with water (2×30 mL) and recrystallized from appropriate solvent.

2,3-Bis(2,5-dimethylthiophen-3-yl)cyclopent-2-en-1-one oxime (2a). Yield 0.58 g (92%), white powder. M.p. = 169–170°C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.87 (s, 3H, Me), 1.91 (s, 3H, Me), 2.36 (s, 3H, Me), 2.40 (s, 3H, Me), 2.89 (s, 4H, $2CH_2$), 6.44 (s, 1H, H^{thioph}), 6.55 (s, 1H, H^{thioph}), 7.56 (br. s, 1H, NOH). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.02, 14.45, 15.15, 15.25, 24.84, 33.89, 125.55 (CH^{thioph}), 126.73 (CH^{thioph}), 130.05, 131.37, 133.94, 134.36, 134.66, 135.56, 135.74, 149.79, 168.01. Mass, m/z (%): 317 (15, $[M]^+$), 300 (59, $[M - OH]^+$), 286 (100, $[M - NOH]^+$). Found, %: S, 63.89; H, 6.14; N, 4.36. $C_{26}H_{31}NOS_2$. Calculated, %: C, 64.32; H, 6.03; N, 4.41.

2-(2,5-Dimethylthiophen-3-yl)-3-phenylcyclopent-2-en-1-one oxime (2b). Yield 0.50 g (89%), beige powder. M.p. = 220–222°C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.94 (s, 3H, Me), 2.44 (s, 3H, Me), 2.82-2.99 (m, 2H, CH_2), 3.00-3.15 (m, 2H, CH_2), 6.54 (s, 1H, H^{thioph}), 7.24-7.27 (m, 5H, CH^{phenyl}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.82, 15.36, 24.40, 32.19, 126.47, 127.44, 128.31, 130.07, 131.45, 133.84, 136.42, 136.52, 151.87, 168.79. Mass, m/z (%): 283 (100, $[M]^+$), 266 (67, $[M - OH]^+$). Found, %: C, 72.23; H, 6.03; N, 4.92; S, 11.34. $C_{17}H_{17}NOS$. Calculated, %: C, 72.05; H, 6.05; N, 4.94; S, 11.31.

3-(4-Bromophenyl)-2-(2,5-dimethylthiophen-3-yl)cyclopent-2-en-1-one oxime (2c). Yield 0.62 g (85%), white powder. M.p. = 253–255°C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.87 (s, 3H, Me), 2.34 (s, 3H, Me), 2.86-2.99 (m, 2H, CH_2), 3.28 (s, 2H, CH_2), 6.47 (s, 1H, H^{thioph}), 7.13 (d, J = 8.8 Hz, 2H, $2H^{phenyl}$), 7.39 (d, J = 8.8 Hz, 2H, $2H^{phenyl}$), 10.51 (s, 1H, NOH). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.06, 14.45, 23.62, 31.08, 120.80, 126.51, 128.42, 130.07, 130.62, 131.07, 132.07, 134.60, 135.01, 148.03, 165.57. Mass, m/z (%): 361, 363 (85, $[M]^+$), 344, 346 (100, $[M - OH]^+$). Found, %: C, 56.45; H, 4.48; Br, 22.11; N, 3.86; S, 8.88. $C_{17}H_{16}BrNOS$. Calculated, %: C, 56.36; H, 4.45; Br, 22.06; N, 3.87; S, 8.85.

2-(2,5-Dimethylthiophen-3-yl)-3-(4-methoxyphenyl)cyclopent-2-en-1-one oxime (2d). Yield 0.58 g (93%), beige powder. M.p. = 218–221°C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.88 (s, 3H, Me^{thioph}), 2.33 (s, 3H, Me^{thioph}), 2.58-3.97 (m, 4H, $2CH_2$), 3.70 (s, 3H, OMe), 6.43 (s, 1H, H^{thioph}), 6.70 (d, *J* = 8.5 Hz, 2H, $2H^{phenyl}$), 7.13 (d, *J* = 8.0 Hz, 2H, $2H^{phenyl}$), 10.10 (s, 1H, NOH). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.02, 14.50, 23.47, 31.13, 54.38 (OCH_3), 112.80, 126.44, 127.80, 128.19, 129.22, 130.55, 132.06, 134.37, 148.89, 158.42, 166.47. Mass, m/z (%): 313 (92, $[M]^+$), 296 (100, $[M – OH]^+$). Found, %: C, 69.15; H, 6.09; N, 4.49; S, 10.26. $C_{18}H_{19}NO_2S$. Calculated, %: C, 68.98; H, 6.11; N, 4.47; S, 10.23.

2-(2,5-Dimethylthiophen-3-yl)-3-(naphthalen-1-yl)cyclopent-2-en-1-one oxime (2e). Yield 0.54 g (81%), yellow crystal. M.p. = 216–218°C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.78 (s, 3H, Me), 2.24 (s, 3H, Me), 2.99-3.10 (m, 4H, $2CH_2$), 6.45 (s, 1H, H^{thioph}), 7.13-7.24 (m, 1H, H^{naph}), 7.34-7.46 (m, 3H, H^{naph}), 7.70-7.85 (m, 3H, H^{naph}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.34, 15.14, 25.18, 35.68, 125.33, 125.53, 125.70, 125.75, 125.82, 126.67, 128.18, 128.38, 129.26, 130.26, 133.63, 134.30, 134.59, 135.42, 135.83, 154.35, 168.06. Mass, m/z (%): 333 (42, $[M]^+$), 316 (100, $[M – OH]^+$). HRMS Calcd for $C_{21}H_{19}NOS$ ($M+H^+$): 334.1260. Found: 334.1263. IR (KBr), cm^{-1}: 3436 (O-H), 3260 (O-H), 2916 (CH_3, $C\text{-}H^{arom}$), 2864 (CH_3, $C\text{-}H^{arom}$), 1624, 1440, 1388, 956, 884, 800 ($C\text{-}H^{arom}$), 776 ($C\text{-}H^{arom}$).

2-(2,5-Dimethylthiophen-3-yl)-3-(2-heptyl-1-benzothiophen-3-yl)cyclopent-2-en-1-one oxime (2f). Yield 0.84 g (96%), white powder. M.p. = 136–137°C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.90 (t, *J* = 6.6 Hz, 3H, CH_3), 1.15–1.35 (m, 8H, $4CH_2$), 1.40–1.56 (m, 1H, ½CH_2), 1.58–1.73 (m, 1H, ½CH_2), 1.79 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.37–2.48 (m, 1H, ½CH_2), 2.50–2.63 (m, 1H, ½CH_2), 2.65–2.80 (m, 1H, ½CH_2), 2.89–3.14 (m, 2H, CH_2), 3.16–3.33 (m, 1H, ½CH_2), 6.50 (s, 1H, H^{thioph}), 7.22–7.36 (m, 2H, H^{arom}), 7.55 (d, *J* = 7.7 Hz, 1H, H^{arom}), 7.70 (br. s, 1H, OH), 7.75 (d, *J* = 7.3 Hz, 1H, H^{arom}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.18, 14.47, 15.20, 22.75, 25.15, 29.23, 29.58, 29.71, 31.25, 31.92, 34.18, 122.21, 122.26, 123.65, 124.16, 126.67, 128.56, 129.21, 134.96, 135.06, 135.44, 138.57, 138.98, 143.57, 150.01, 168.04. Mass, m/z (%): 437 (17, $[M]^+$), 420 (98, $[M–OH]^+$), 322 (100, $(M–C_7H_{14}–OH]^+$). Found, %: S, 70.70; H, 7.28; N, 3.18. $C_{26}H_{31}NOS_2$. Calculated, %: C, 71.35; H, 7.14; N, 3.20.

3-(2,5-Dimethylthiophen-3-yl)-2-phenylcyclopent-2-en-1-one oxime (2g). Yield 0.43 g (76%), beige powder. M.p. = 178–181°C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.78 (s, 3H, Me), 2.37 (s, 3H, Me), 2.80-2.89 (m, 2H, CH_2), 2.91-3.01 (m, 2H, CH_2), 6.49 (s, 1H, H^{thioph}), 7.18-7.32 (m, 5H, CH^{phenyl}), 7.35 (br. s, 1H, NOH). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.35, 15.19, 25.11, 34.28, 125.83, 127.37, 128.19, 129.36, 133.43, 134.05, 134.15, 135.95, 136.13,

149.96, 167.83. Mass, m/z (%): 283 (100, $[M]^+$), 268 (49, $[M - CH_3]^+$), 252 (24, $[M - CH_3 - OH]^+$). Found, %: C, 72.25; H, 6.01; N, 4.93; S, 11.35. $C_{17}H_{17}NOS$. $C_{17}H_{17}NOS$. Calculated, %: C, 72.05; H, 6.05; N, 4.94; S, 11.31.

3-(2,5-Dimethylthiophen-3-yl)-2-(naphthalen-1-yl)cyclopent-2-en-1-one oxime (2h). Yield 0.64 g (96%), pale yellow powder. M.p. = 145–148°C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.82 (s, 3H, Me), 2.22 (s, 3H, Me), 2.83-3.15 (m, 4H, $2CH_2$), 6.32 (s, 1H, H^{thioph}), 7.23 (m, 1H, H^{naph}), 7.31-7.52 (m, 3H, H^{naph}), 7.68-7.89 (m, 3H, H^{naph}), 8.06 (br. s, 1H, NOH). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.95, 15.00, 25.03, 34.29, 125.47, 125.65, 125.94, 126.00, 127.69, 128.16, 128.25, 131.33, 132.21, 133.25, 133.67, 134.96, 135.11, 145.40, 151.38, 168.42. Mass, m/z (%): 333 (37, $[M]^+$), 316 (100, $[M - OH]^+$). Found, %: C, 75.74; H, 5.72; N, 4.18; S, 9.64.$C_{21}H_{19}NOS$. Calculated, %: C, 75.64; H, 5.74; N, 4.20; S, 9.62.

3-(2,5-Dimethylthiophen-3-yl)-2-(2-methyl-1-benzothiophen-3-yl)cyclopent-2-en-1-one oxime (2i). Yield 0.40 g (57%), white powder. M.p. = 175–177°C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.82 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.86–3.24 (m, 4H, $2CH_2$), 6.38 (s, 1H, CH^{thioph}), 7.14-7.30 (m, 2H, $CH^{benzthioph}$), 7.43 (m, 1H, $CH^{benzthioph}$), 7.72 (m, 1H, $CH^{benzthioph}$). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.67, 14.91, 15.05, 24.95, 34.17, 121.78, 122.86, 123.48, 123.82, 125.38, 126.14, 129.99, 133.53, 135.17, 135.80, 138.16, 138.33, 139.21, 152.29. Mass, m/z (%): 353 (53, $[M]^+$), 336 (100, $[M - OH]^+$). Found, %: C, 68.12; H, 5.44; N, 3.97; S, 18.11. $C_{20}H_{19}NOS_2$. Calculated, %: C, 67.95; H, 5.42; N, 3.96; S, 18.14.

2,3-Bis(2-methyl-1-benzothiophen-3-yl)cyclopent-2-en-1-one oxime (2j). Yield 0.55 g (71%), light-brown powder. M.p. = 103–104°C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.69-2.23 (m, 6H, $2CH_3$), 2.85–3.29 (m, 2H, CH_2), 3.42–3.67 (m, 2H, CH_2), 6.72-7.45 (m, 5H, $CH^{benzthioph}$), 7.52-7.89 (m, 3H, $CH^{benzthioph}$), 8.92 (br. s, 1H, OH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 14.58, 14.98, 25.07, 33.65, 121.68, 122.12, 122.25, 123.36, 123.75, 124.01, 124.15, 126.11, 127.85, 128.04, 129.15, 130.17, 131.36, 136.94, 137.10, 137.35, 139.01, 155.09, 164.90. Mass, m/z (%): 389 (94, $[M]^+$), 372 (100, $[M–OH]^+$), 357 (78, $(M–CH_3–OH]^+$). Found, %: C, 71.09; H, 4.90; N, 3.62; S, 16.49. $C_{23}H_{19}NOS_2$. Calculated, %: C, 70.92; H, 4.92; N, 3.60; S, 16.46.

Ketoximes 3 (general method). To cooled (12 °C) solution of DCP **1** (3.0 mmol) and fresh-prepared *n*-butyl nitrite (3.6 mmol) in dioxane (15 mL) conc. hydrochloric acid (0.36 mL) was added dropwise and solution was stirred at room temperature for 2 h. The reaction mixture was poured into cold water (100 mL) and extracted with ethyl acetate (3×30 mL), combined organic phases were washed with water (50 mL), dried with magnesium sulfate and evaporated

in vacuum. The residue was purified by column chromatography eluting by petrol. ester / ethyl acetate 2:1 and recrystallized from appropriate solvent.

3,4-Bis(2,5-dimethylthiophen-3-yl)cyclopent-3-ene-1,2-dione 1-oxime (3a). Yield 0.72 g (73%), dark-green crystals. M.p. = 154–156°C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.93 (s, 3H, Me), 1.98 (s, 3H, Me), 2.40 (s, 6H, 2Me), 3.70 (s, 2H, CH_2), 6.53 (s, 1H, H^{thioph}), 6.58 (s, 1H, H^{thioph}), 9.02 (br. s, 1H, NOH). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.42, 15.19, 15.26, 15.39, 32.58 (CH_2), 125.29 (CH^{thioph}), 126.58 (CH^{thioph}), 128.61, 132.94, 135.95, 136.30, 137.22, 137.80, 139.72, 153.13, 157.77, 190.87 (C=O). Mass, m/z (%): 331 (63, $[M]^+$), 314 (100, $[M - OH]^+$). HRMS Calcd for $C_{17}H_{17}NNaO_2S_2$ ($M+Na^+$): 354.0593. Found: 354.0587. IR (KBr), cm^{-1}: 3380 (O-H), 2952 (CH_3, C-H^{thioph}), 2912 (CH_3, C-H^{thioph}), 1704 (C=O), 1648 (C=N), 1600, 1560, 1496, 1444, 1300, 908, 740.

3-(2,5-Dimethylthiophen-3-yl)-4-phenylcyclopent-3-en-1,2-dione 1-oxime (3b). Yield 0.65 g (73%), orange powder. M.p. = 103–105°C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.97 (s, 3H, Me), 2.43 (s, 3H, Me), 3.72 (s, 1H, ½CH_2), 3.81 (s, 1H, ½CH_2), 6.51 (s, 1H, H^{thioph}), 7.31-7.59 (m, 5H, CH^{phenyl}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.11, 15.29, 30.80, 125.63, 126.10, 127.93, 128.21, 128.66, 128.81, 129.00, 131.07, 134.56, 135.33, 136.90, 137.95, 160.22, 191.11 (C=O). Mass, m/z (%): 297 (31, $[M]^+$), 280 (100, $[M - OH]^+$). Found, %: C, 68.72; H, 5.05; N, 4.72; S, 10.80. $C_{17}H_{15}NO_2S_2$. Calculated, %: C, 68.66; H, 5.08; N, 4.71; S, 10.78.

3-(2,5-Dimethylthiophen-3-yl)-4-(naphthalen-1-yl)cyclopent-3-en-1,2-dione 1-oxime (3c). Yield 0.67 g (64%), pale yellow powder. M.p. = 190–191°C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.77 (s, 3H, Me), 2.25 (s, 3H, Me), 3.90 (s, 2H, CH_2), 6.41 (s, 1H, H^{thioph}), 7.32-7.42 (m, 2H, H^{naph}), 7.43-7.53 (m, 2H, H^{naph}), 7.63 (d, *J* = 8.5 Hz, 1H, H^{naph}), 7.86 (t, *J* = 8.5 Hz, 2H, H^{naph}), 10.11 (br. s, 1H, NOH). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.50, 15.06, 33.75, 125.12, 125.31, 125.53, 126.15, 126.35, 126.46, 127.32, 128.64, 129.19, 130.09, 133.67, 134.23, 135.94, 136.26, 140.94, 153.09, 162.37, 190.60 (C=O). Mass, m/z (%): 347 (19, $[M]^+$), 329 (100, $[M - H_2O]^+$), 261 (380, $[M - C(O)C(NOH)CH_2]^+$). Found, %: C, 71.89; H, 5.00; N, 3.99; S, 9.28. $C_{21}H_{17}NO_2S$. Calculated, %: C, 72.60; H, 4.93; N, 4.03; S, 9.23. IR (KBr), cm^{-1}: 3336 (O-H), 3045 (CH_3, C-H^{arom}), 2918 (CH_3, C-H^{arom}), 2854 (CH_3, C-H^{arom}), 1711 (C=O), 1651, 1424, 1358, 1307, 1266, 963, 901, 812, 784 (C-H^{naph}), 776 (C-H^{naph}).

3-(2,5-Dimethylthiophen-3-yl)-4-(2-methyl-1-benzothiophen-3-yl)cyclopent-3-en-1,2-dione 1-oxime (3d). Yield 0.68 g (62%), green powder. M.p. = 120–122°C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.84 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 3.85 (br.s,

2H, CH_2), 6.48 (s, 1H, CH^{thioph}), 7.23-7.39 (m, 2H, $CH^{benzthioph}$), 7.49-7.60 (m, 1H, $CH^{benzthioph}$), 7.70-7.87 (m, 1H, $CH^{benzthioph}$), 9.74 (br. s, 1H, NOH). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.52, 15.13, 15.20, 32.28, 122.08, 122.29, 124.28, 124.76, 126.02, 127.56, 128.23, 136.13, 136.46, 137.96, 138.64, 140.03, 141.23, 153.02, 157.61, 190.50 (C=O). Mass, m/z (%): 367 (91, $[M]^+$), 350 (78, $[M–OH]^+$), 309 (100, $(M–NOH]^+$), 282 (100, $(M–C(O)C(NOH)CH_2]^+$). HRMS Calcd for $C_{20}H_{17}NO_2S_2$ ($M+Na^+$): 390.0593. Found: 390.0592. IR (KBr), cm^{-1}: 3378 (O-H), 3290 (O-H), 3045 (CH_3, C-H^{arom}), 2912 (CH_3, C-H^{arom}), 2854 (CH_3, C-H^{arom}), 1704 (C=O), 1648, 1604, 1492, 1460, 1436, 1388, 1300, 1286, 1016, 992, 896, 772 (C-$H^{benzthioph}$), 748 (C-$H^{benzthioph}$), 732 (C-$H^{benzthioph}$).

3-(2,5-Dimethylthiophen-3-yl)-4-(2-heptyl-1-benzothiophen-3-yl)cyclopent-3-en-1,2-dione 1-oxime (3e). Yield 1.14 g (84%), green amorphous powder. M.p. = 59–60°C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.89 (t, *J* = 5.9 Hz, 3H, CH_3), 1.16–1.35 (m, 9H, $4CH_2$ + ½CH_2), 1.40–1.56 (m, 1H, ½CH_2), 1.82 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.33–2.45 (m, 1H, ½CH_2), 2.46–2.63 (m, 1H, ½CH_2), 3.54 (d, *J* = 22.7 Hz, 1H, ½CH_2), 4.14 (d, *J* = 22.7 Hz, 1H, ½CH_2), 6.47 (s, 1H, H^{thioph}), 7.27–7.39 (m, 2H, H^{arom}), 7.55 (d, *J* = 7.0 Hz, 1H, H^{arom}), 7.78 (d, *J* = 7.3 Hz, 1H, H^{arom}), 11.05 (br. s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.14, 14.64, 15.12, 22.70, 29.15, 29.66, 29.89, 31.13, 31.84, 32.60, 122.07, 122.46, 124.23, 124.75, 126.13, 127.31, 127.37, 136.10, 136.54, 137.85, 138.75, 141.19, 146.09, 152.85, 158.36, 190.74 (C=O). Mass, m/z (%): 451 (12, $[M]^+$), 435 (80, $[M – O]^+$), 336 (100, $(M – C_7H_{14} – OH]^+$). Found, %: C, 71.62; H, 6.01; N, 2.87; S, 13.19. $C_{29}H_{29}NO_2S_2$. Calculated, %: C, 71.42; H, 5.99; N, 2.87; S, 13.15.

4-(2,5-Dimethylthiophen-3-yl)-3-phenylcyclopent-3-en-1,2-dione 1-oxime (3f). Yield 0.62 g (70%), brown powder. M.p. = 85–88°C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.84 (s, 3H, Me), 2.40 (s, 3H, Me), 3.66 (s, 2H, CH_2), 6.59 (s, 1H, H^{thioph}), 7.31-7.41 (m, 5H, CH^{phenyl}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 15.03, 15.16, 30.01, 125.21, 128.13, 128.45, 128.89, 129.03, 130.96, 131.89, 132.14, 132.35, 137.46, 138.54, 158.06, 167.79, 190.80 (C=O). Mass, m/z (%): 297 (100, $[M]^+$), 212 (71, $[M – C(O)C(NOH)CH_2]^+$). Found, %: C, 68.69; H, 5.10; N, 4.71; S, 10.76. $C_{17}H_{15}NO_2S_2$. Calculated, %: C, 68.66; H, 5.08; N, 4.71; S, 10.78.

4-(2,5-Dimethylthiophen-3-yl)-3-(2-methyl-1-benzothiophen-3-yl)cyclopent-3-en-1,2-dione 1-oxime (3g). Yield 0.52 g (47%), dark-green powder. M.p. = 105–107°C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.95 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.86 (s, 2H, CH_2), 6.51 (s, 1H, CH^{thioph}), 7.13-7.39 (m, 3H, $CH^{benzthioph}$), 7.74 (m, 1H, $CH^{benzthioph}$), 10.22 (br. s, 1H, NOH). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 15.06, 15.14, 15.40, 32.73, 121.90,

122.51, 123.80, 124.14, 124.58, 125.09, 132.41, 136.36, 137.15, 138.36, 138.71, 139.62, 140.66, 152.91, 160.04, 190.18. Mass, m/z (%): 367 (100, $[M]^+$), 350 (100, $[M - OH]^+$), 282 (49, $(M - C(O)C(NOH)CH_2]^+$), 267 (44, $(M - CH_3 - C(O)C(NOH)CH_2]^+$). Found, %: C, 65.46; H, 4.67; N, 3.81; S, 17.40. $C_{20}H_{17}NO_2S_2$. Calculated, %: C, 65.37; H, 4.66; N, 3.81; S, 17.45.

3,4-Bis(2-methyl-1-benzothiophen-3-yl)cyclopent-3-en-1,2-dione 1-oxime (3h). Yield 0.59 g (49%), brown powder. M.p. = 137–139°C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.13 (s, 6H, $2CH_3$), 2.19–2.24 (m, 2H, CH_2), 7.04-7.37 (m, 5H, $H^{benzthioph}$), 7.54–7.68 (m, 3H, $H^{benzthioph}$). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 15.40, 20.71, 32.74, 121.85, 121.94, 122.33, 123.46, 123.77, 124.07, 124.34, 124.48, 124.66, 124.81, 127.81, 137.74, 138.20, 138.39, 138.53, 140.80, 152.47, 160.77, 176.69, 189.82 (C=O). Mass, m/z (%): 403 (100, $[M]^+$), 387 (32, $[M - CH_4]^+$), 317 (28, $(M - C(O)C(NOH)CH_2]^+$). Found, %: C, 68.50; H, 4.23; N, 3.47; S, 15.91. $C_{23}H_{17}NO_2S_2$. Calculated, %: C, 68.46; H, 4.25; N, 3.47; S, 15.89.

Dioximes 4 (general method). The suspension of ketoxime **3** (0.50 mmol), hydroxylamine hydrochloride (10.0 mmol) and anhydrous sodium acetate (10.0 mmol) in abs. ethanol (3 mL) was refluxed for 10 h and poured into crushed ice (40 mL). The residue was filtered off, washed with water (2×20 mL), purified by column chromatography eluting by petrol. ester / ethyl acetate 3:1 and recrystallized from appropriate solvent.

3,4-Bis(2,5-dimethylthiophen-3-yl)cyclopent-3-ene-1,2-dione dioxime (4a). Yield 61.0 mg (35%), light-yellow powder. M.p. = 179–183°C (ethanol). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 1.83 (s, 3H, Me), 1.95 (s, 3H, Me), 2.30 (s, 3H, Me), 2.32 (s, 3H, Me), 3.53 (s, 2H, CH_2), 6.53 (s, 1H, H^{thioph}), 6.61 (s, 1H, H^{thioph}), 11.63 (s, 1H, NOH), 11.78 (s, 1H, NOH). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 13.70, 14.05, 14.78, 14.81, 35.70, 125.98 (CH^{thioph}), 127.50 (CH^{thioph}), 130.67, 132.52, 133.11, 133.44, 134.10, 134.14, 135.19, 139.26, 151.78, 152.39. Mass, m/z (%): 346 (17, $[M]^+$), 329 (61, $[M - OH]^+$), 311 (65, $[M - 2OH - H]^+$), 297 (35, $[M - NOH - OH - H]^+$). HRMS (ESI): Found, m/z: 347.0876, 369.0690. $C_{17}H_{18}N_2O_2S_2$. Calculated, m/z: 347.0882 $[M + H]^+$, 369.0702 $[M + Na]^+$. IR (KBr), cm^{-1}: 3210 (O-H), 2916 (CH_3, C-H^{thioph}), 1424 (C=N), 1456 (C=N), 952 (N=O).

3-(2,5-Dimethylthiophen-3-yl)-4-(naphthalen-1-yl)cyclopent-3-en-1,2-dione dioxime (4b). Yield 69.0 mg (38%), yellow powder. M.p. = 181–182°C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.80 (s, 3H, Me), 2.28 (s, 3H, Me), 3.87 (s, 2H, CH_2), 6.54 (s, 1H, CH^{thioph}), 7.29 (d, J = 6.8 Hz, 1H, CH^{naph}), 7.35-7.48 (m, 3H, CH^{naph}), 7.71-7.90 (m, 3H, CH^{naph}), 9.11 (br. s, 1H, NOH), 11.97 (br. s, 1H, NOH). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.43, 15.07, 37.12, 125.37, 125.43, 126.01, 126.08, 126.34, 126.58, 128.53, 128.73, 128.88, 130.34, 133.73, 134.48,

135.35, 135.41, 135.77, 144.12, 153.07, 153.12. Mass, m/z (%): 362 (52, $[M]^+$), 345 (100, $[M - OH]^+$), 328 (87, $[M - 2OH]^+$). Found, %: C, 69.65; H, 5.03; N, 7.73; S, 8.71. $C_{21}H_{18}N_2O_2S$. Calculated, %: C, 69.59; H, 5.01; N, 7.73; S, 8.85. IR (KBr), cm^{-1}: 3201 (br., O-H), 2918 (CH_3, C-H^{arom}), 2856 (CH_3, C-H^{arom}), 1438 (C=N), 1415, 1385, 1009, 956 (N=O), 797 (C-H^{arom}), 775 (C-H^{arom}), 750 (C-H^{arom}).

3-(2,5-Dimethylthiophen-3-yl)-4-(2-methyl-1-benzothiophen-3-yl)cyclopent-3-en-1,2-dione dioxime (4c). Yield 69.0 mg (36%), green powder. M.p. = 129–132°C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.81 (s, 3H, Me), 2.14 (s, 3H, Me), 2.30 (s, 3H, Me), 3.46-4.02 (m, 2H, CH_2), 6.56 (s, 1H, H^{thioph}), 7.24-7.39 (m, 2H, $H^{benzothioph}$), 7.54 (d, *J* = 7.3 Hz, 1H, $H^{benzothioph}$), 7.73 (d, *J* = 7.0 Hz, 1H, $H^{benzothioph}$), 9.17 (br. s, 1H, NOH), 12.41 (br. s, 1H, NOH). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.41, 15.01, 15.07, 35.40, 122.11, 122.19, 123.90, 124.41, 126.35, 128.25, 129.08, 135.59, 135.89, 136.41, 138.41, 138.48, 138.85, 139.10, 152.59, 152.71. Mass, m/z (%): 382 (22, $[M]^+$), 365 (100, $[M - OH]^+$), 348 (87, $[M - 2OH]^+$). HRMS (ESI): Found, m/z: 383.0898, 405.0705, 421.0443. $C_{20}H_{18}N_2O_2S_2$. Calculated, m/z: 383.0882 $[M + H]^+$, 405.0702 $[M + Na]^+$, 421.0441 $[M + K]^+$. IR (KBr), cm^{-1}: 2275 (O-H), 2916 (CH_3, C-H^{thioph}), 1432 (C=N), 1456 (C=N), 960 (N=O).

Acetyloximes 5, 6 (general method). To solution of monooxime **2** or ketoxime **3** (1 mmol) in anhydrous pyridine (4 mL) acetic anhydride was added, reaction mixture was stirred at room temperature for 3 h, poured into diluted solution of hydrochloric acid in water (70 mL) and extracted with methylene chloride (3×20 mL), combined organic phases were washed with water (30 mL), dried with sodium sulfate and evaporated in vacuum. The residue was recrystallized from appropriate solvent.

***N*-(Acetyloxy)-2,3-bis(2,5-dimethylthiophen-3-yl)cyclopent-2-en-1-imine (5a).** Yield 0.28 g (78%), light-brown powder. M.p. = 47–49°C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.88 (s, 3H, CH_3^{thioph}), 1.91 (s, 3H, CH_3^{thioph}), 2.21 (m, 3H, CH_3^{Ac}), 2.37 (s, 6H, $2CH_3^{thioph}$), 2.87–3.01 (m, 4H, $2CH_2$), 6.45 (s, 1H, CH^{thioph}), 6.57 (s, 1H, CH^{thioph}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.31, 14.42, 15.14, 15.29, 19.94 (CH_3^{Ac}), 26.51, 33.96, 125.39, 126.93, 129.16, 130.50, 133.52, 135.20, 135.41, 135.84, 136.19, 154.59, 169.80, 174.53. Mass, m/z (%): 359 (9, $[M]^+$), 301 (100, $[M - OAc]^+$), 286 (20, $(M - NOAc]^+$). HRMS (ESI): Found, m/z: 382.0909. $C_{22}H_{21}NO_2S_2$. Calculated, m/z: 382.0906 $[M + Na]^+$. IR (KBr), cm^{-1}: 2962 (CH_3, C-H^{thioph}), 2917 (CH_3, C-H^{thioph}), 2856 (CH_3, C-H^{thioph}), 1760 (br., C=O, C=N), 1614, 1440, 1364, 1261, 1213 (C-O), 1199, 1141, 1095, 1021, 944 (N-O), 821, 800.

***N*-(Acetyloxy)-3-(2,5-dimethylthiophen-3-yl)-2-(2-methyl-1-benzothiophen-3-yl)cyclopent-2-en-1-imine (5b).** Yield 0.28 g (71%), brown powder. M.p. = 98–100°C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.81 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.26 (m, 6H, $2CH_3$), 2.98–3.22 (m, 4H, $2CH_2$), 6.40 (s, 1H, CH^{thioph}), 7.06-7.42 (m, 3H, $CH^{benzthioph}$), 7.59-7.86 (m, 1H, $CH^{benzthioph}$). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.67, 15.00, 15.17, 19.91 (CH_3^{Ac}), 26.59, 34.22, 121.67, 122.88, 123.46, 123.66, 125.18, 125.26, 125.65, 128.98, 133.11, 136.22, 136.38, 138.25, 138.90, 139.03, 156.96, 170.32, 173.69. Mass, m/z (%): 395 (16, $[M]^+$), 336 (88, $[M - OAc]^+$), 322 (63, $(M - NOAc]^+$). HRMS (ESI): Found, m/z: 334.0612. $C_{22}H_{21}NO_2S_2$. Calculated, m/z: 434.0645 $[M + K]^+$. IR (KBr), cm^{-1}: 2918 (CH_3, C-H^{arom}), 2852 (CH_3, C-H^{arom}), 1759 (C=O), 1665 (C=N), 1614, 1434, 1365, 1299, 1206 (C-O), 1177, 1001, 942 (N-O), 761 (C-H^{arom}), 732 (C-H^{arom}).

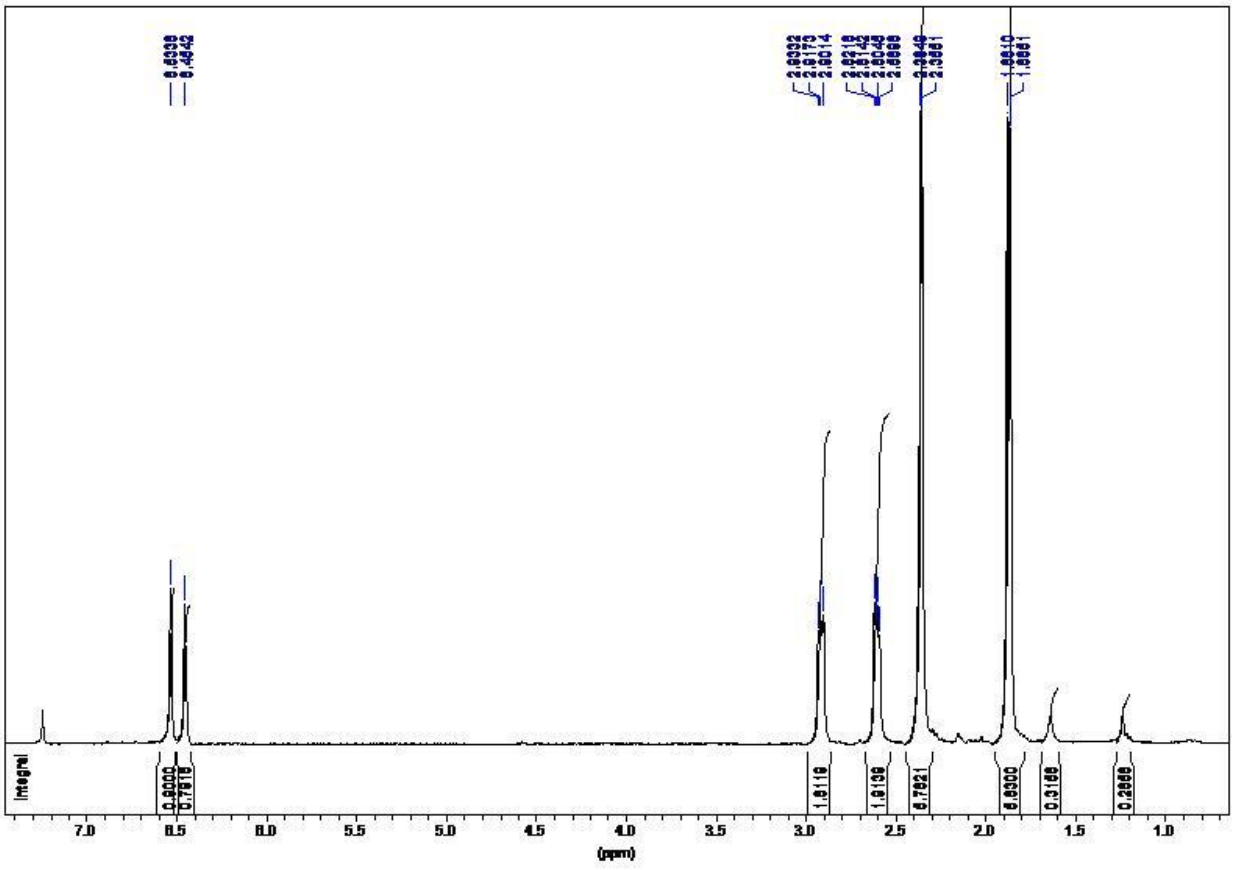
***N*-(Acetyloxy)-2,3-bis(2-methyl-1-benzothiophen-3-yl)cyclopent-2-en-1-imine (5c).** Yield 0.33 g (76%), light-brown powder. M.p. = 66–67°C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.78-2.16 (m, 6H, $2CH_3^{benzthioph}$), 2.17 (s, 3H, CH_3^{Ac}), 2.72–3.47 (m, 4H, $2CH_2$), 7.07-7.45 (m, 4H, $CH^{benzthioph}$), 7.56-7.80 (m, 1H, $CH^{benzthioph}$). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 15.11, 15.56, 19.96 (CH_3^{Ac}), 26.98, 34.18, 121.68, 121.93, 122.18, 123.47, 123.57, 123.88, 124.31, 124.39, 133.25, 138.02, 138.17, 138.40, 138.52, 138.55, 138.59, 138.88, 139.43, 139.48, 173.20, 173.23. Mass, m/z (%): 431 (19, $[M]^+$), 373 (100, $[M - OAc]^+$), 356 (55, $(M - NOAc - H_2]^+$). HRMS (ESI): Found, m/z: 454.0904. $C_{25}H_{21}NO_2S_2$. Calculated, m/z: 454.0906 $[M + Na]^+$. IR (KBr), cm^{-1}: 3058 (CH_3, C-H^{arom}), 2957 (CH_3, C-H^{arom}), 2922 (CH_3, C-H^{arom}), 2853 (CH_3, C-H^{arom}), 1757 (C=O), 1618, 1457, 1433, 1364, 1205 (C-O), 1176, 1000, 934 (N-O), 759 (C-H^{arom}), 731 (C-H^{arom}).

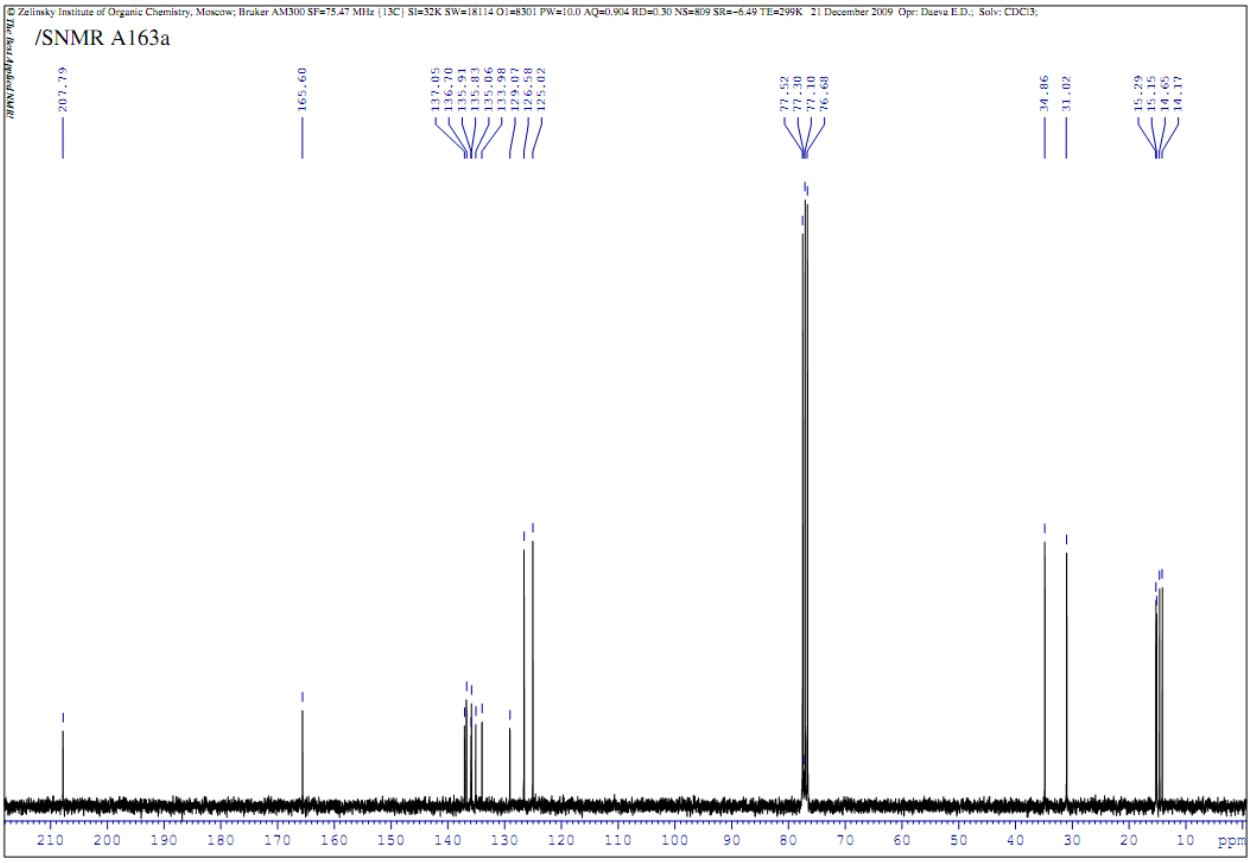
5-[(Acetyloxy)imino]-2,3-bis(2,5-dimethylthiophen-3-yl)cyclopent-2-en-1-one (6a). Yield 0.33 g (88%), dark-brown powder. M.p. = 143–145°C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.95 (s, 3H, Me), 1.97 (s, 3H, Me), 2.36 (s, 3H, Me), 2.40 (s, 6H, 2Me), 3.76 (s, 2H, CH_2), 6.50 (s, 1H, H^{thioph}), 6.57 (s, 1H, H^{thioph}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.34, 15.12, 15.24, 19.79 (CH_3^{Ac}), 33.66, 124.86, 126.23, 127.97, 132.27, 136.26, 136.47, 137.51, 138.18, 140.43, 157.47, 169.49 (C=O), 188.70 (C=O). Mass, m/z (%): 373 (9, $[M]^+$), 314 (72, $[M - OAc]^+$), 300 (46, $[M - NOAc]^+$), 270 (89, $[M - NOAc - 2CH_3]^+$). HRMS (ESI): Found, m/z: 396.0710. $C_{19}H_{19}NO_3S_2$. Calculated, m/z: 396.0700 $[M + Na]^+$. IR (KBr), cm^{-1}: 2916 (CH_3, C-H^{thioph}), 2854 (CH_3, C-H^{thioph}), 1787 (C=O^{Ac}), 1707 (C=O), 1654 (C=N), 1598, 1563, 1496, 1444, 1388, 1366, 1302, 1262, 1196 (C-O), 1168, 1005, 941 (N-O), 868, 803.

5-[(Acetyloxy)imino]-3-(2,5-dimethylthiophen-3-yl)-2-(2-methyl-1-benzothiophen-3-yl)cyclopent-2-en-1-one (6b). Yield 0.36 g (89%), dark-green powder. M.p. = 100–102°C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.92 (s, 3H, Me), 2.22 (s, 3H, Me), 2.30 (s, 3H, Me), 2.38 (s, 3H, Me), 3.93 (s, 2H, CH_2), 6.52 (s, 1H, H^{thioph}), 7.12-7.31 (m, 3H, $CH^{benzthioph}$), 7.72 (d, *J* = 5.6 Hz, 1H, $CH^{benzthioph}$). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 15.00, 15.13, 15.38, 19.76 (CH_3^{Ac}), 33.66, 121.93, 122.30, 123.87, 124.06, 124.15, 124.81, 131.97, 136.80, 137.52, 138.31, 138.42, 140.01, 140.42, 157.23, 159.84 (C=O), 188.22 (C=O). Mass, m/z (%): 409 (19, $[M]^+$), 351 (100, $[M - OAc]^+$), 337 (30, $[M - NOAc]^+$), 282 (47, $[M - C(O)C(NOAc)CH_2]^+$), 267 (34, $[M - C(O)C(NOAc)CH_2 - CH_3]^+$). HRMS (ESI): Found, m/z: 432.0691. $C_{22}H_{19}NO_3S_2$. Calculated, m/z: 432.0700 $[M + Na]^+$. IR (KBr), cm^{-1}: 2955 (CH_3, $C\text{-}H^{arom}$), 2919 (CH_3, $C\text{-}H^{arom}$), 2853 (CH_3, $C\text{-}H^{arom}$), 1777 ($C{=}O^{Ac}$), 1709 (C=O), 1651 (C=N), 1600, 1529, 1434, 1367, 1201 (C-O), 1176, 931 (N-O), 859, 756 ($C\text{-}H^{arom}$), 730 ($C\text{-}H^{arom}$).

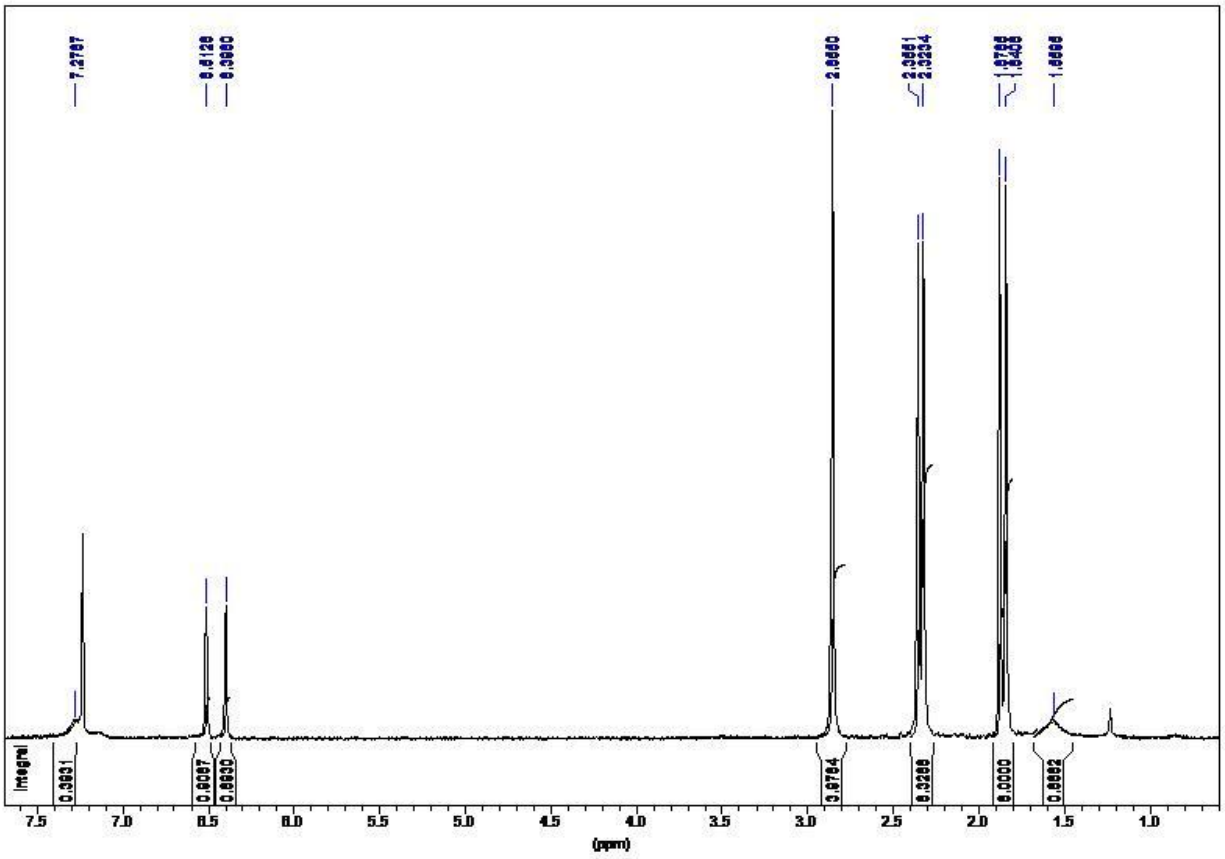
Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds 1a, 2a, 3a, 4a, 5a and 6a

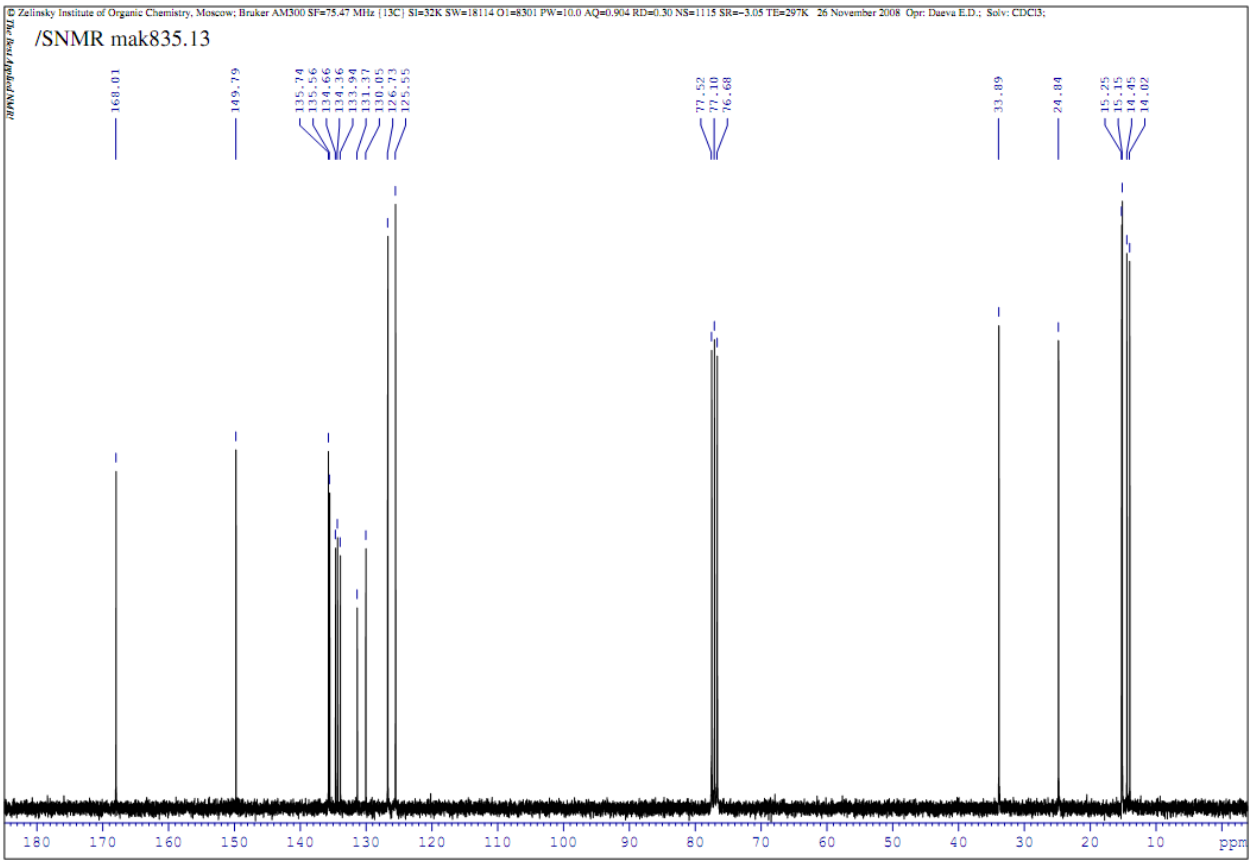
2,3-Bis(2,5-dimethylthiophen-3-yl)cyclopent-2-en-1-one **1a.**



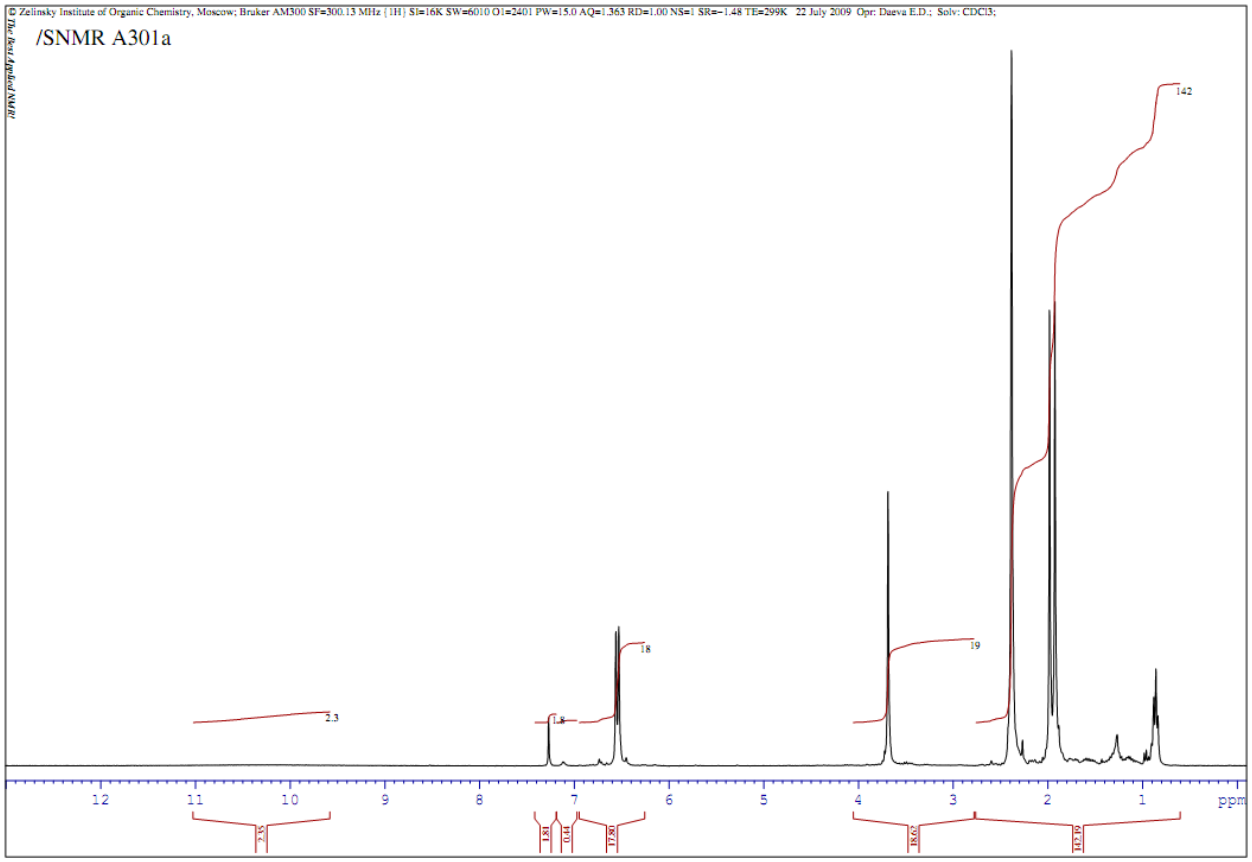


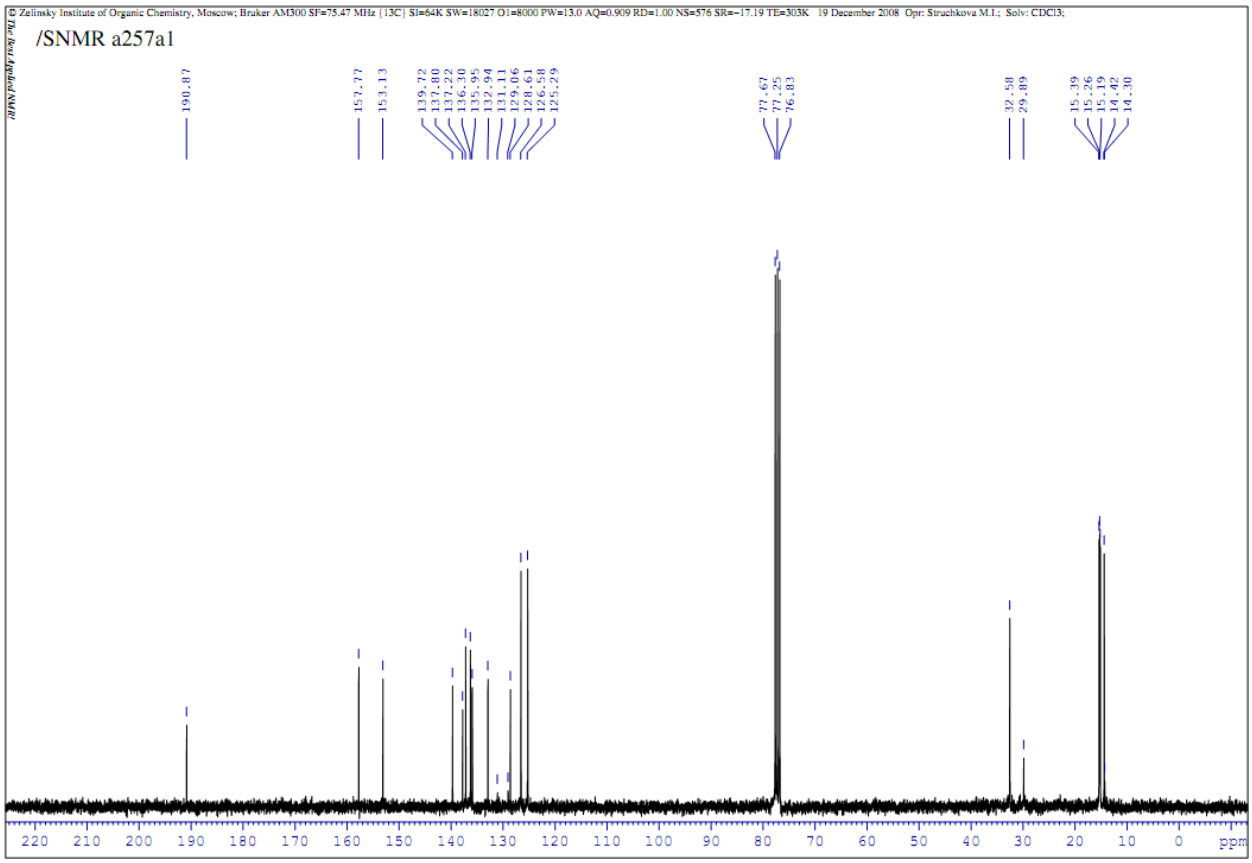
2,3-Bis(2,5-dimethylthiophen-3-yl)cyclopent-2-en-1-one oxime **2a.**



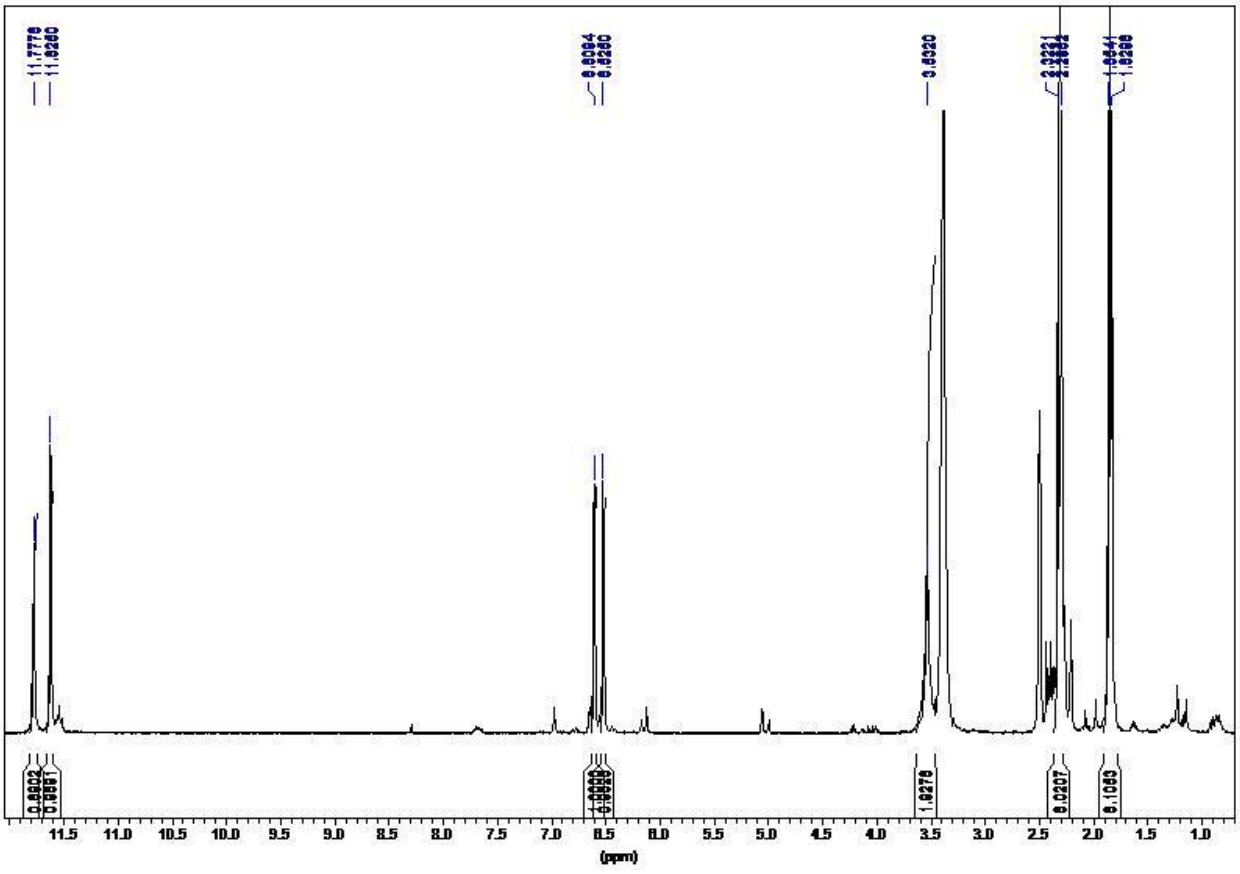


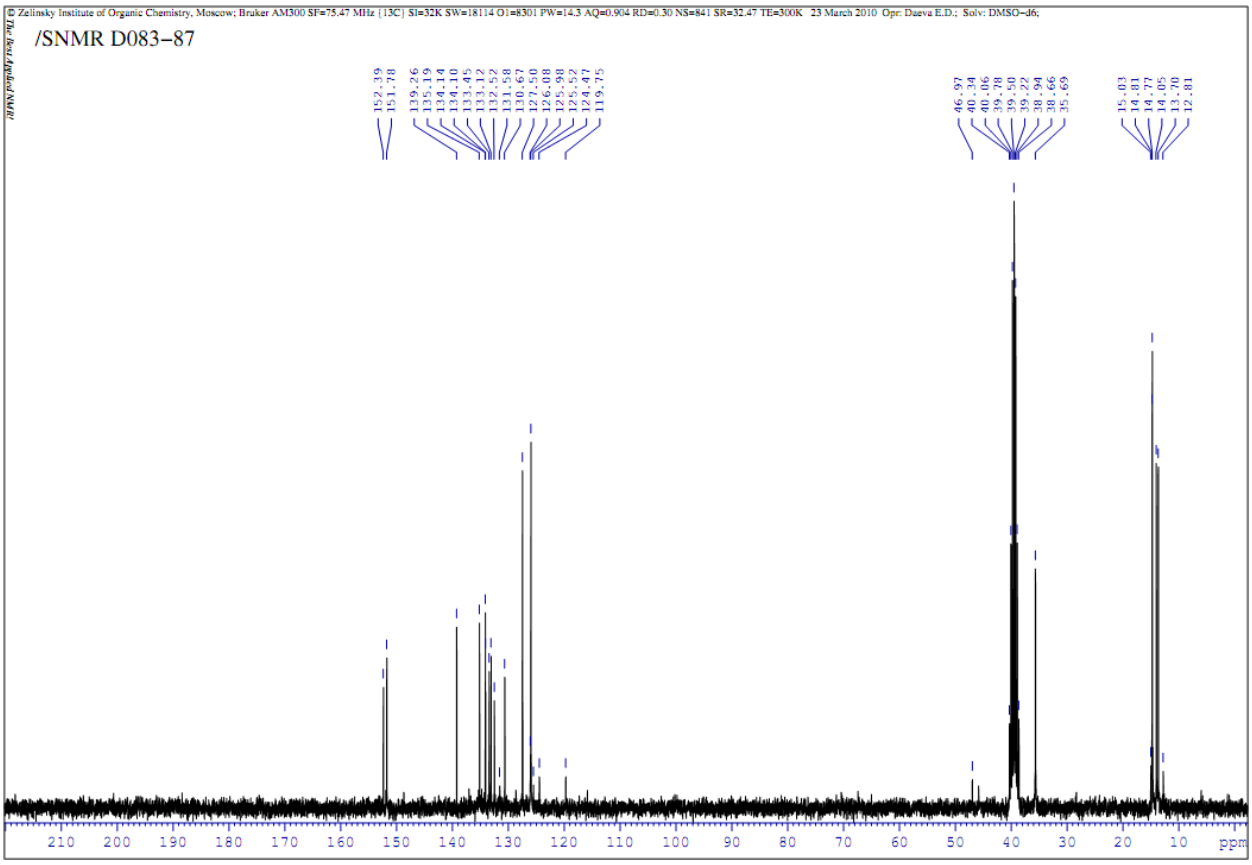
3,4-Bis(2,5-dimethylthiophen-3-yl)cyclopent-3-ene-1,2-dione 1-oxime **3a.**



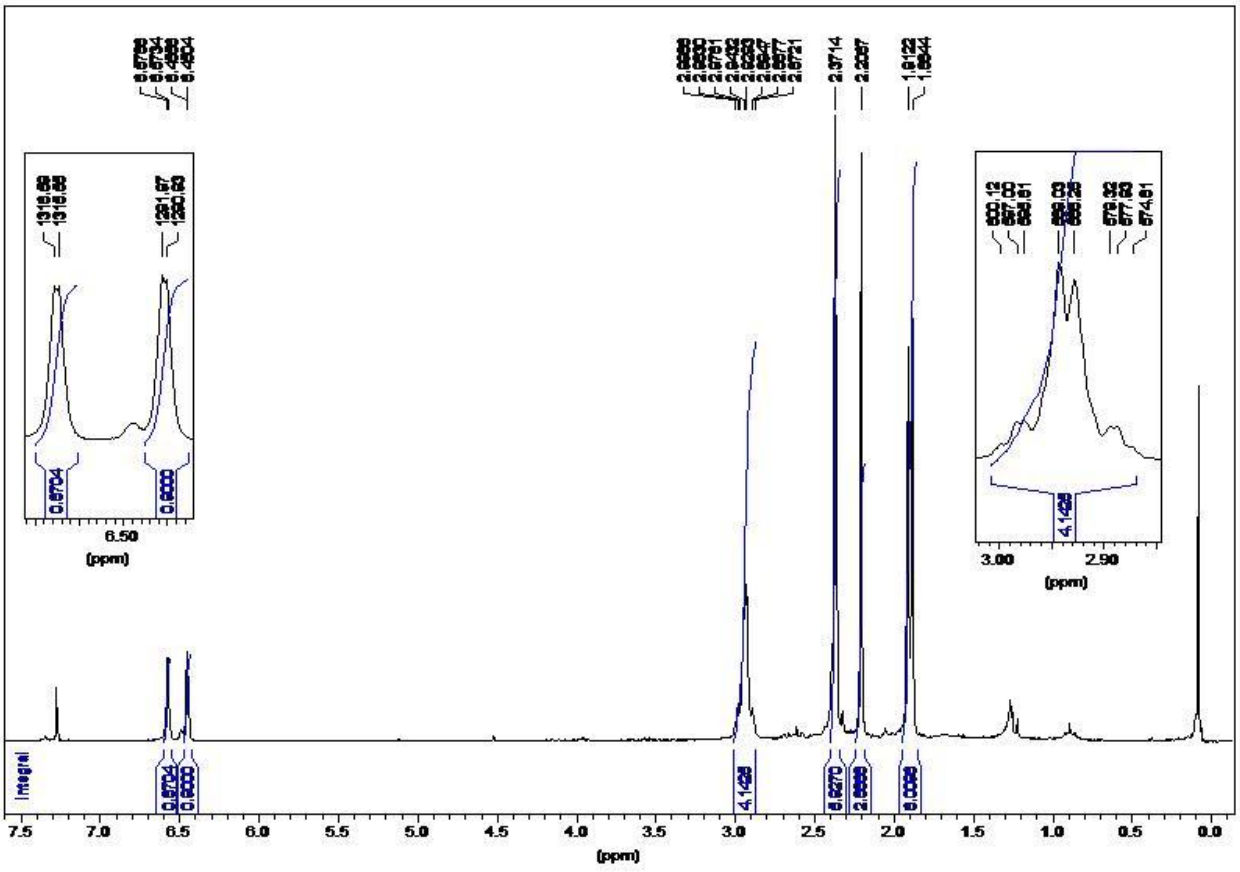


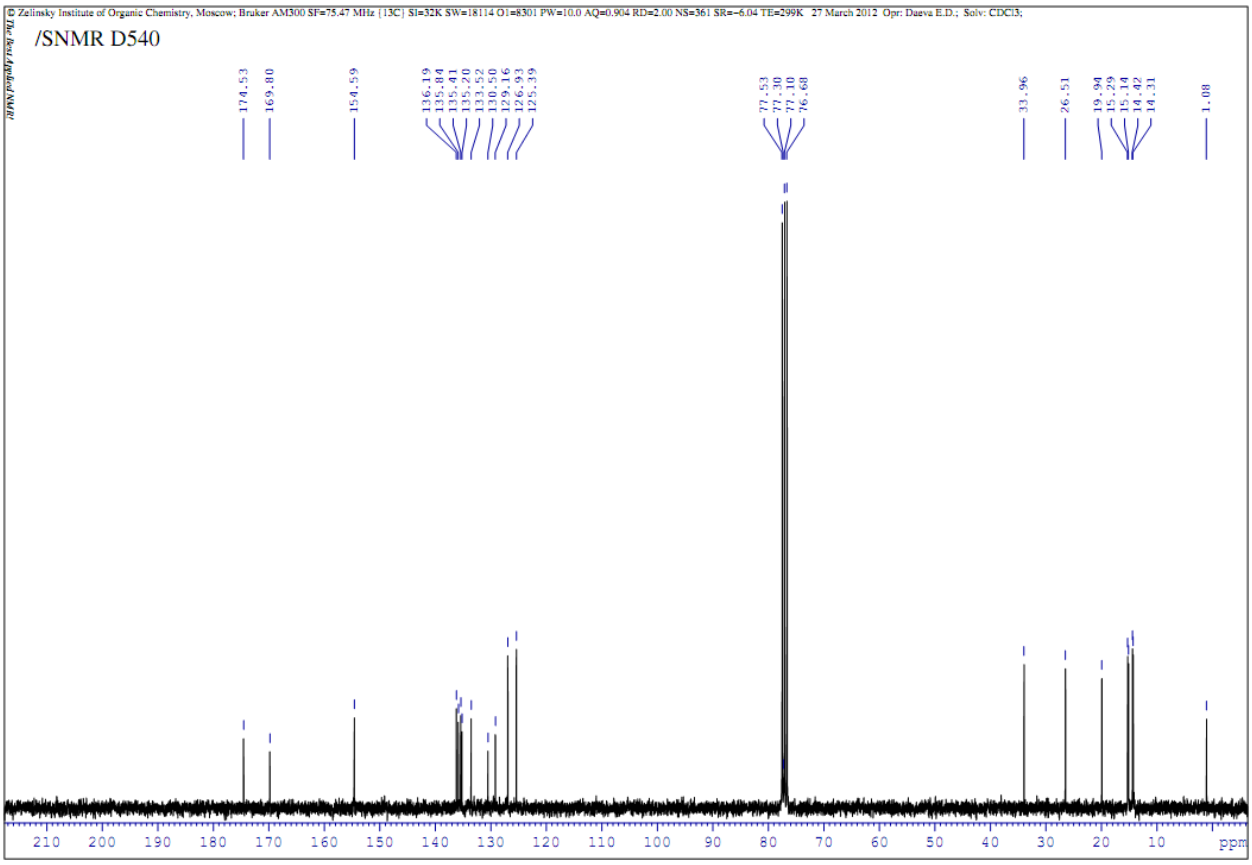
3,4-Bis(2,5-dimethylthiophen-3-yl)cyclopent-3-ene-1,2-dione dioxime **4a.**



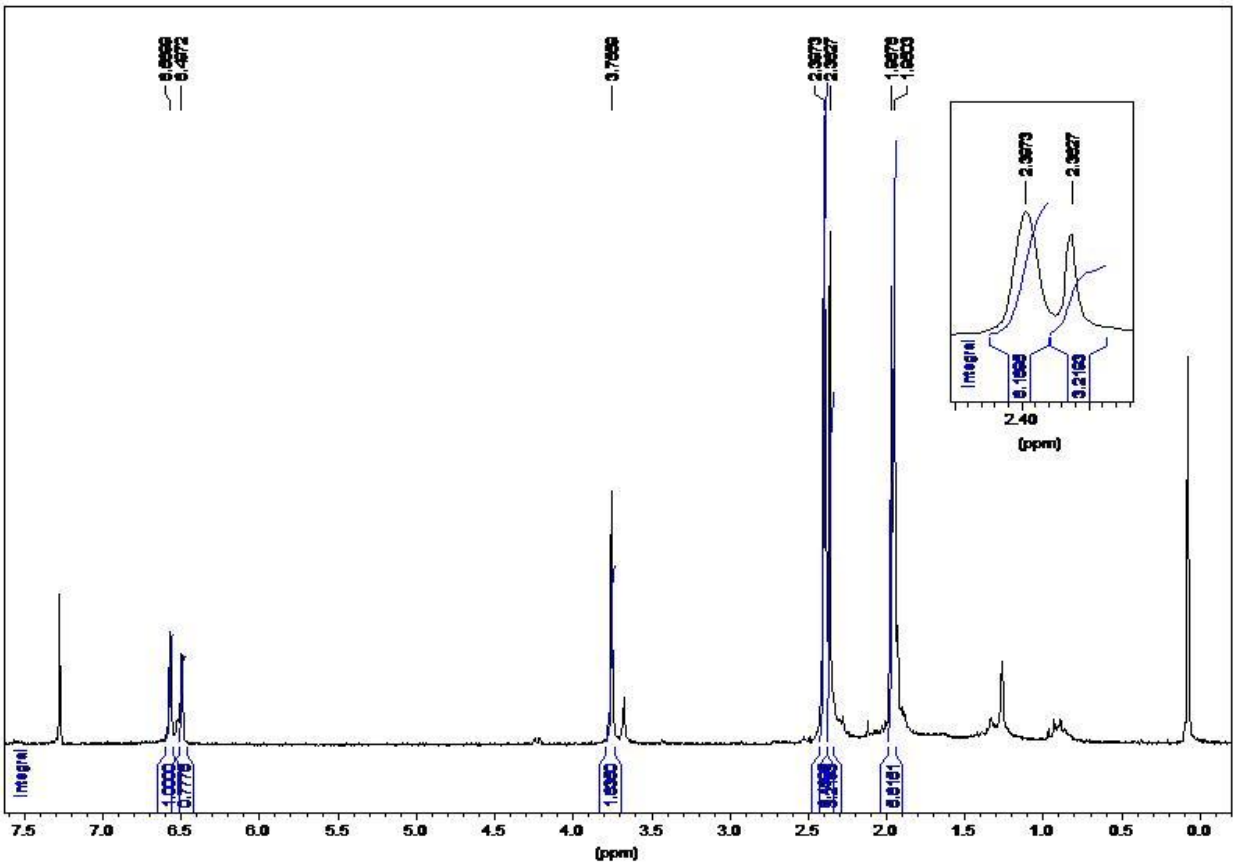


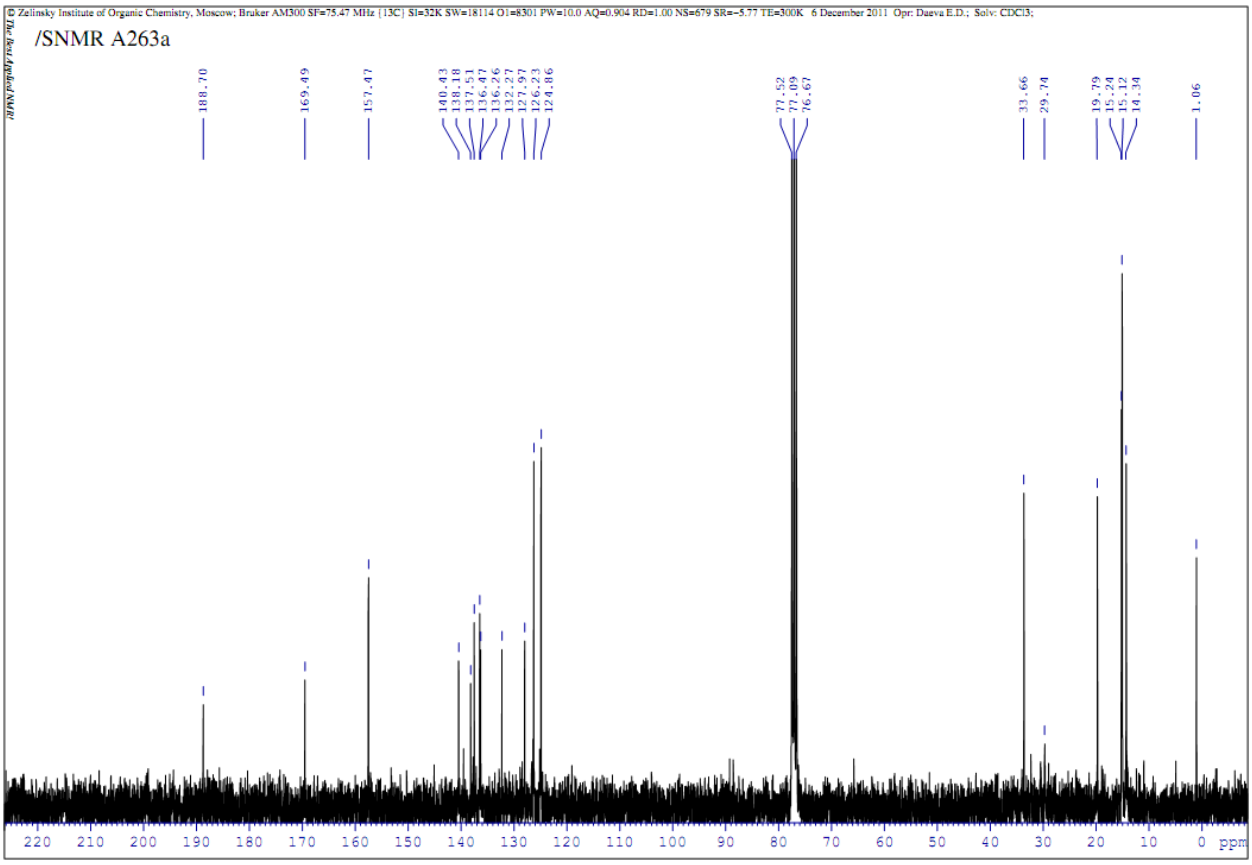
N-(Acetyloxy)-2,3-bis(2,5-dimethylthiophen-3-yl)cyclopent-2-en-1-imine **5a.**





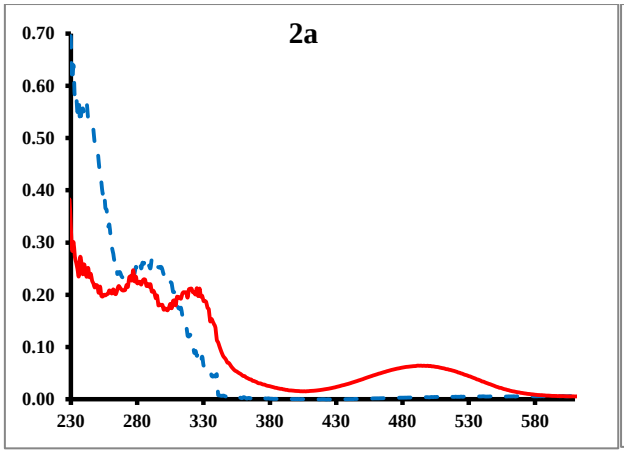
5-[(Acetyloxy)imino]-2,3-bis(2,5-dimethylthiophen-3-yl)cyclopent-2-en-1-one **6a.**

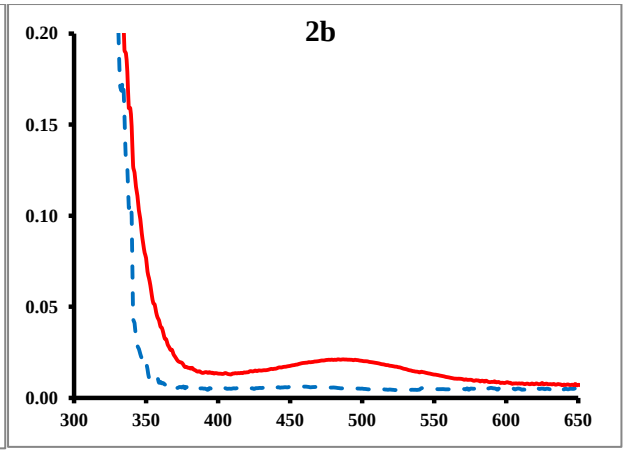


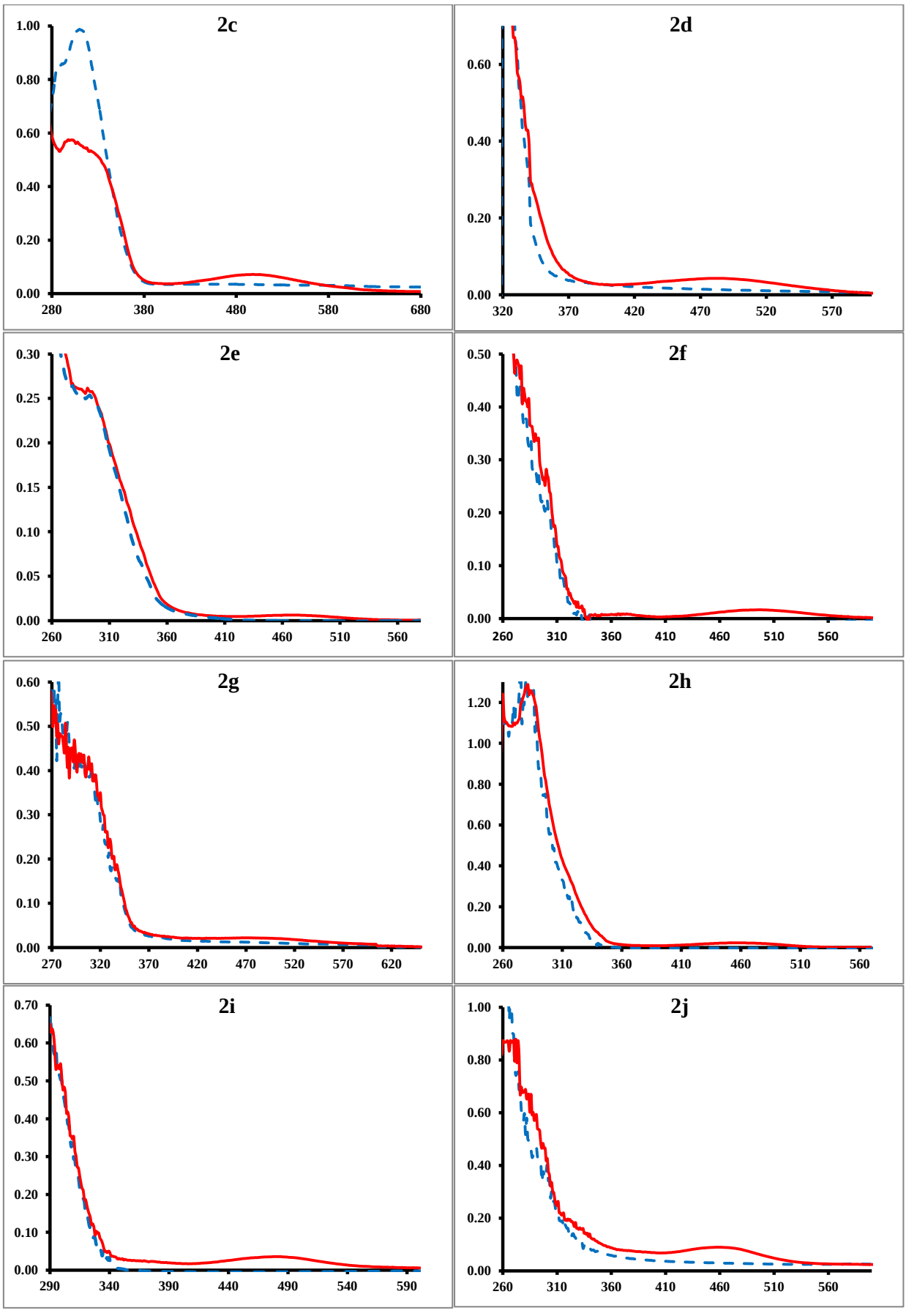


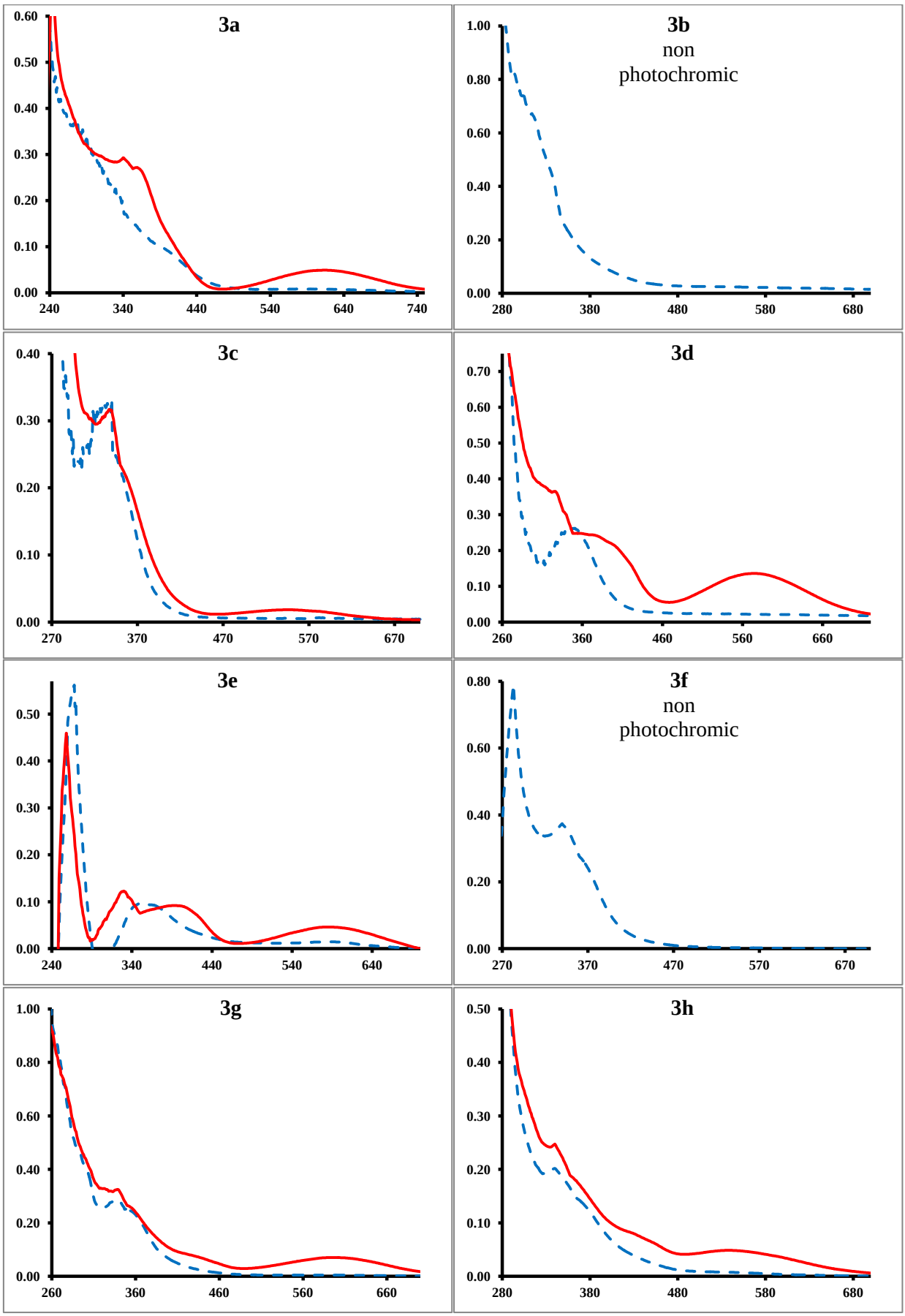
Absorption spectra of oxime derivatives 2-6

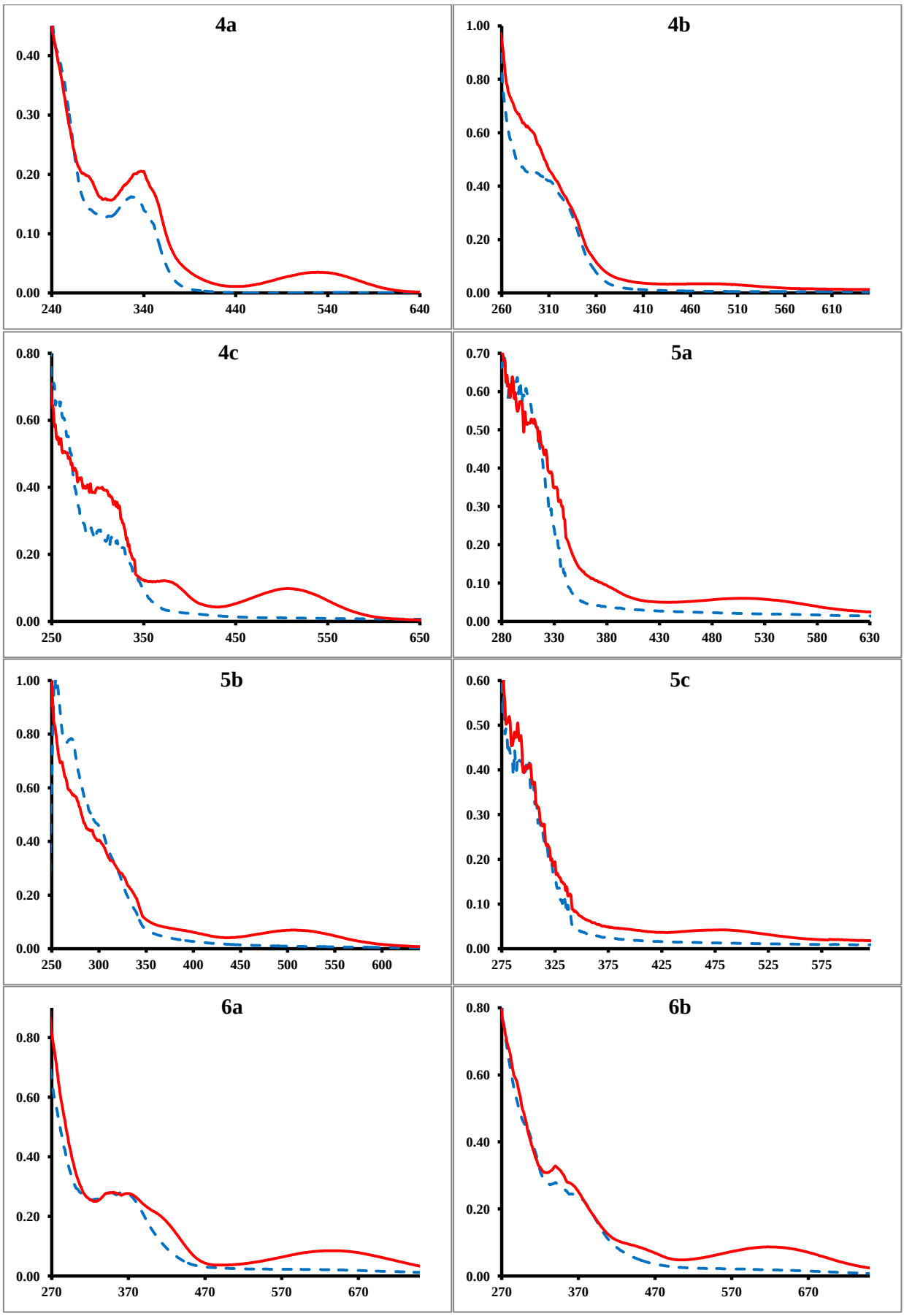
Figures below show the absorption spectra of acetonitrile solutions ($C = 2.0 \cdot 10^{-5}$ mol·L^{-1}) of 2,3-diarylcyclopent-2-en-1-one oxime derivatives **2-6** obtained at 293 K in the presence of air. The initial (uncolored) state **A** (dotted blue lines) and photostationary state **PSS** (solid red lines) obtained by UV irradiation at 365 nm are shown in each figure.











Comparative table of properties of compounds 1a, 2a, 3a, 4a, 5a and 6a

Entry	Compound	λ_A, nm (ε_A, L·mol^{-1}·cm^{-1})*	λ_B, nm (ε_B, L·mol^{-1}·cm^{-1})**	$\varphi_{A\rightarrow B}$ #	$\varphi_{B\rightarrow A}$ ##	n¶	$\tau_{1/2\ therm}^{B\rightarrow A}$ ¶¶, h
1	**1a**	208 ($1.64\cdot10^4$), 245 ($1.46\cdot10^4$), 309 ($6.43\cdot10^3$)	547 ($1.11\cdot10^4$)	0.27	0.065	50	939
2	**2a**	287 ($4.54\cdot10^4$)	494 ($3.50\cdot10^4$)	0.40	0.004	300	282
3	**3a**	339 ($1.83\cdot10^4$), 350 ($1.62\cdot10^4$)	611 ($1.50\cdot10^4$)	0.08	0.027	12	1107
4	**4a**	234 ($2.96\cdot10^4$) 324 ($7.21\cdot10^3$)	521 ($1.75\cdot10^4$)	0.10	0.003	70	690
5	**5a**	303 ($3.12\cdot10^4$)	508 ($1.60\cdot10^4$)	0.14	0.004	< 10	2.0
6	**6a**	357 ($1.78\cdot10^4$)	395 ($1.09\cdot10^4$), 626 ($1.42\cdot10^4$)	0.07	0.002	< 10	209

* – wavelength of absorption band maximum (molar extinction coefficient) of colorless form **A**, ** – wavelength of absorption band maximum (molar extinction coefficient) of colored form **B**, # – quantum yield of photocoloration reaction, ## – quantum yield of photobleaching reaction, ¶ – number of photocoloration-photobleaching cycles leading to destruction of 20% of compound at 293 K (values more than 20 cycles are obtained by extrapolation of experimental data), ¶¶ – time for which the concentration of colored form **B** decrease by 50% in dark at 293 K (obtained by means of processing of kinetics curves).

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