Aerobic Dimerization of Ethyl 4-Thienyl-3-Ketobutanoate towards a Modifiable Photochromic Diarylethene Precursor

Andrey G. Lvov,¹* Nikita A. Milevsky,² Anna M. Yanina,³ Vadim V. Kachala,¹ Valerii Z. Shirinian ¹

¹N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47, Leninsky prosp., 119991 Moscow, Russian Federation,
e-mail: lvov-andre@yandex.ru, lvov-andre@ioc.ac.ru
²Moscow Chemical Lyceum, 4, Tamozhenniy Proezd, 111033 Moscow, Russian Federation
³Mendeleev University of Chemical Technology of Russia, Miusskaya Sq., 9, Moscow, 125047, Russian Federation

Table of contents

I. Easily modifiable photochromic diarylethene precursors .................................................. S2
II. Synthesis and characterization of new compounds ............................................................ S6
   II.1. General information ................................................................................................................ S6
   II.2. Synthesis of diarylethene 1 ..................................................................................................... S7
   II.3. Chemical modifications of diarylethene 1 ............................................................................. S8
III. Comparison of photochromic properties of diarylenes V and 1 ...................................... S16
IV. 2D NMR data ........................................................................................................................ S17
   IV.1. Diarylethene 1 ....................................................................................................................... S17
   IV.2. Diarylethene 8 ...................................................................................................................... S23
V. Copies of NMR spectra .......................................................................................................... S30
VI. Copies of HRMS spectra ......................................................................................................... S47
I. Easily modifiable photochromic diarylethene precursors

Scheme S1. Main modifications of diarylethene I.
Scheme S2. Main modifications of diarylethene II.


R = Si, S, B, P, Br derivatives

≈ 9 examples

≈ 5 examples

≈ 13 derivatives via 1-2 steps

≈ 19 examples
Scheme S3. Main modifications of diarylethene III.

- ≈ 60 derivatives via 1-2 steps
- ≈ 120 derivatives via 1-3 steps
- ≈ 12 derivatives via 1-2 steps
- ≈ 20 derivatives via 1-2 steps
- 2 derivatives (Hal = I, Br) via 1 step
- ≈ 5 examples (R = P, Si, S, B derivatives) via 1 step

Scheme S4. Main modifications of diarylethene IV.

Org. Lett., 2009, 11, 3890

Scheme S5. Main modifications of diarylethene V.

Mendeleev Commun., 2013, 23, 268
Dyes Pigm., 2016, 124, 258


Photochem. Photobiol. Sci., 2013, 12, 1717

II. Synthesis and characterization of new compounds
II.1. General information

Experimental Procedures. NMR spectra were recorded in deuterated solvents on spectrometers working at 300.13, 600.13 MHz for $^1$H and 75.77, 150.91 MHz for $^{13}$C. 2D spectra were set using standard parameters. Both $^1$H and $^{13}$C NMR chemical shifts are referenced relative to the residual solvents signals (CHCl$_3$: $\delta$ 7.27 for $^1$H NMR and $\delta$ 77.2 for $^{13}$C NMR; DMSO-d$_6$: $\delta$ 2.50 for $^1$H NMR) and reported in parts per million (ppm) at 293 K. Data are represented as follows: chemical shift, multiplicity (s, singlet; d, doublet; m, multiplet; t, triplet; br, broad), coupling constant in hertz (Hz), integration, and assignment. Melting points (mp) were recorded using an apparatus and not corrected. High-resolution mass spectra were obtained from a TOF mass spectrometer with an ESI source. All chemicals and anhydrous solvents were purchased from commercial sources and used without further purification. Silica column chromatography was performed using silica gel 60 (70–230 mesh); TLC analysis was conducted on silica gel 60 F$_{254}$ plates.


Photochemical Studies. UV−vis spectra were recorded in 1.0 cm quartz cuvettes. The experimental measurements were performed in the presence of air in solutions of acetonitrile.
II.2. Synthesis of diarylethene 1

Scheme S6.

General procedure.
To a solution of ketoester 2 (4.17 mmol, 1.00 g) in ethanol (see Table S1 for details) a water solution of KOH (entries 1-3, 6-10) or KOH (entries 4,5) was added. The resulting mixture was refluxed until completion of reaction (TLC control). The mixture was poured into water (200 mL) and extracted with ethyl acetate (5 × 50 mL). The combined organic phases were washed with brine (100 mL), dried over MgSO₄, and evaporated in vacuum. The residue was purified by column chromatography by eluting with petroleum ester/ethyl acetate (4:1).

Table S1. Conditions for 1 gram-scale experiments.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Solvent</th>
<th>Yield 1</th>
<th>Time, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KOH  (5 equiv, 1%*)</td>
<td>EtOH/H₂O (1:1)</td>
<td>40%</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>KOH  (5 equiv, 3.5%)</td>
<td>EtOH/H₂O (1:1)</td>
<td>57%</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>KOH  (5 equiv, 10%)</td>
<td>EtOH/H₂O (1:1)</td>
<td>32%</td>
<td>16</td>
</tr>
<tr>
<td>4</td>
<td>KOH  (5 equiv, 3.5%)</td>
<td>EtOH (96%)</td>
<td>35%</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>KOH  (5 equiv, 3.5%)</td>
<td>EtOH (abs.)</td>
<td>10%</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>NaOH (5 equiv, 3.5%)</td>
<td>EtOH/H₂O (1:1)</td>
<td>38%</td>
<td>19</td>
</tr>
<tr>
<td>7</td>
<td>LiOH (5 equiv, 3.5%)</td>
<td>EtOH/H₂O (1:1)</td>
<td>39%</td>
<td>26</td>
</tr>
<tr>
<td>8</td>
<td>KOH (2 equiv, 3.5%)</td>
<td>EtOH/H₂O (1:1)</td>
<td>42%</td>
<td>53</td>
</tr>
<tr>
<td>9</td>
<td>KOH (10 equiv, 3.5%)</td>
<td>EtOH/H₂O (1:1)</td>
<td>30%</td>
<td>23</td>
</tr>
<tr>
<td>10</td>
<td>KOH (5 equiv, 3.5%)</td>
<td>18-crown-6 (0.05 eq) EtOH/H₂O (1:1)</td>
<td>36%</td>
<td>29</td>
</tr>
</tbody>
</table>

* Concentration for total mixture of the solvents

2,3-Bis(2,5-dimethylthiophen-3-yl)-4-hydroxy-4-methylcyclopent-2-enone (1).

Gray powder; mp 159-161 °C (ethanol).

1H NMR (300 MHz, CDCl₃) δ = 1.52 (s, 3H, CH₃), 1.76 (s, 3H, CH₃), 1.92 (s, 3H, CH₃), 2.24 (br s, 1H, OH), 2.36 (s, 3H, CH₃), 2.46 (s, 3H, CH₃), 2.77 (d, J = 18.3 Hz, 1H, ½CH₂), 2.82 (d, J = 18.3 Hz, 1H, ½CH₂), 6.43 (s, 1H, Hthiophene), 6.95 (s, 1H, Hthiophene).

1H NMR (300 MHz, DMSO-d₆) δ = 1.28 (s, 3H, CH₃), 1.68 (s, 3H, CH₃), 1.84 (s, 3H, CH₃), 2.30 (s, 3H, CH₃), 2.39 (s, 3H, CH₃), 2.60 (d, J = 18.1 Hz, 1H, ½CH₂), 2.70 (d, J = 18.1 Hz, 1H, ½CH₂), 5.58 (br s, 1H, OH), 6.36 (s, 1H, Hthiophene), 7.03 (s, 1H, Hthiophene).

13C NMR (75 MHz, CDCl₃) δ = 14.1, 14.3, 15.2 (2C), 27.4, 51.5, 76.8, 125.0, 126.3, 127.6, 130.2, 135.7, 135.9, 136.5, 136.7, 137.3, 167.5, 204.1.

HRMS (ESI-TOF) m/z [M + H]+ calcd for C₁₈H₂₆O₂S₂ 333.0977, found 333.0972.
2 gram scale experiment in the optimized conditions.

To a solution of ketoester 2 (8.33 mmol, 2.00 g) in ethanol (31 mL) was added a solution of KOH (41.67 mmol, 2.33 g) in water (31 mL). The resulting mixture was refluxed for 35 h. The mixture was poured into water (300 mL) and extracted with ethyl acetate (5 x 50 mL). The combined organic phases were washed with brine (100 mL), dried over MgSO_4, and evaporated in vacuum. The residue was purified by column chromatography by eluting with petroleum ester/ethyl acetate (4:1) to give 816 mg (59%) of diarylethene 1.

II.3. Chemical modifications of diarylethene 1

2,3-Bis(2,5-dimethylthiophen-3-yl)-4-methylenecyclopent-2-enone (5).

A solution of triflic acid (0.33 mmol, 30 µL) in abs. CH_2Cl_2 (2 mL) was added dropwise to a solution of diarylethene 1 (0.30 mmol, 100 mg) in abs. CH_2Cl_2 (2 mL) at 0 °C. The resulting mixture was stirred for 0.5 h at room temperature, poured into water (100 mL) and extracted with CH_2Cl_2 (2 x 30 mL). The combined organic phases were washed with 5% NaHCO_3 (50 mL) and water (50 mL), dried over MgSO_4, and evaporated in vacuum. Light brown labile powder, 95% yield (90 mg).

^1H NMR (300 MHz, CDCl_3) δ = 1.89 (s, 6H, CH_3), 2.37 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 3.26 (s, 2H, CH_2), 5.27-5.43 (m, 2H, =CH_2), 6.43 (s, 1H, H_thiophene), 6.52 (s, 1H, H_thiophene).

^13C NMR (75 MHz, CDCl_3) δ = 14.1, 14.3, 15.1, 15.2, 40.2, 112.3, 126.1, 126.3, 128.0, 129.9, 135.7, 136.2 (2C), 136.5, 139.7, 143.4, 160.5, 203.2.

HRMS (ESI-TOF) m/z [M + H]^+ calcld for C_{18}H_{18}O_2S_3 315.0868, found 315.0872.

2,3-Bis(2,5-dimethylthiophen-3-yl)-4-((phenylthio)methyl)cyclopent-2-enone (6) and 2,3-bis(2,5-dimethylthiophen-3-yl)-4-hydroxy-4-((phenylthio)methyl)cyclopent-2-enone (7).

Method A. To a solution of freshly prepared diarylethene 5 (0.32 mmol, 100 mg) in abs. CH_2Cl_2 (4 mL) triethylamine (0.64 mmol, 90 µL) and thiophenol (0.48 mmol, 50 µL) were added and the solution was stirred at room temperature until completion of reaction (TLC control). The resulting mixture was poured into water (100 mL) and extracted with CH_2Cl_2 (2 x 30 mL). The combined organic phases were washed with water (50 mL), dried over MgSO_4, and evaporated in vacuum. The residue was purified by column chromatography by eluting with petroleum ester/ethyl acetate (4:1 -> 1:1).

Method B. Reaction was performed according method A under inert atmosphere (argon).
2,3-Bis(2,5-dimethylthiophen-3-yl)-4-((phenylthio)methyl)cyclopent-2-enone (6).

Gray powder; 27% yield (36 mg, method A), 73% yield (99 mg, method B); mp 125-127 °C.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta = 1.79$ (s, 3H, CH$_3$), 1.88 (s, 3H, CH$_3$), 2.38 (s, 3H, CH$_3$), 2.42 (s, 3H, CH$_3$), 2.58 (dd, $J = 18.9, 2.1$ Hz, 1H, $\frac{1}{2}$CH$_2$), 2.74 (dd, $J = 12.8, 9.0$ Hz, 1H, $\frac{1}{2}$CH$_2$), 2.84 (dd, $J = 18.9, 6.8$ Hz, 1H, $\frac{1}{2}$CH$_2$), 3.24 (dd, $J = 12.8, 2.9$ Hz, 1H, $\frac{1}{2}$CH$_2$), 3.46-3.57 (m, 1H, CH), 6.44 (s, 1H, H$_{thiophene}$), 6.45 (s, 1H, H$_{thiophene}$), 7.17-7.37 (m, 5H, H$_{arom}$).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta = 14.2$ (2C), 15.2 (2C), 38.7, 40.5, 41.7, 124.2, 126.3, 126.6, 128.4, 129.0 (2C), 130.3 (2C), 131.8, 135.3, 135.8 (2C), 137.3, 137.5 (2C), 166.7, 205.7.

HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for C$_{24}$H$_{26}$OS$_3$ 425.1062, found 425.1051.

2,3-Bis(2,5-dimethylthiophen-3-yl)-4-hydroxy-4-((phenylthio)methyl)cyclopent-2-enone (7).

Brown powder; 49% yield (68 mg, method A); mp 149-151 °C.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta = 1.75$ (s, 3H, CH$_3$), 1.92 (s, 3H, CH$_3$), 2.36 (s, 3H, CH$_3$), 2.45 (s, 3H, CH$_3$), 2.63 (d, $J = 18.4$ Hz, 1H, $\frac{1}{2}$CH$_2$), 2.84 (d, $J = 18.4$ Hz, 1H, $\frac{1}{2}$CH$_2$), 3.21 (d, $J = 12.9$ Hz, 1H, $\frac{1}{2}$CH$_2$), 3.32 (d, $J = 12.9$ Hz, 1H, $\frac{1}{2}$CH$_2$), 6.46 (s, 1H, H$_{thiophene}$), 7.01 (s, 1H, H$_{thiophene}$), 7.19-7.40 (m, 5H, H$_{arom}$).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta = 14.3$, 14.4, 15.2 (2C), 44.2, 48.9, 79.0, 125.2, 126.2, 127.0, 127.6, 129.2 (2C), 129.7, 130.3 (2C), 135.5, 135.8, 136.3, 126.8, 138.1, 138.3, 164.4, 203.5.

HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for C$_{24}$H$_{26}$O$_2$S$_3$ 441.1011, found 441.0994.

2,3-Bis(2,5-dimethylthiophen-3-yl)-4-((morpholinomethyl)cyclopent-2-enone (8).

Freshly prepared diarylethene 5 (0.32 mmol, 100 mg) was dissolved in morpholine (2 mL) and the solution was stirred at room temperature for 3 days. The resulting mixture was poured into water (100 mL) and extracted with ethyl acetate (2 × 30 mL). The combined organic phases were washed with water (50 mL), dried over MgSO$_4$, and evaporated in vacuum. The residue was purified by flash-chromatography by eluting with petroleum ester/ethyl acetate (2:1 -> 1:1).

Brown amorphous powder; 65% yield (83 mg).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta = 1.82$ (s, 3H, CH$_3$), 1.88 (s, 3H, CH$_3$), 2.24-2.30 (m, 1H, $\frac{1}{2}$CH$_2$), 2.37 (s, 3H, CH$_3$), 2.43 (s, 3H, CH$_3$), 2.43-2.48 (m, 2H, CH$_2$), 2.53-2.65 (m, 4H, $\frac{1}{2}$CH$_2$+$\frac{1}{2}$CH$_2$+CH$_2$), 2.82 (dd, $J = 18.9, 6.6$ Hz, 1H, $\frac{1}{2}$CH$_2$), 3.50-3.56 (m, 1H, CH), 3.70-3.78 (m, 4H, CH$_2$), 6.42 (s, 1H, H$_{thiophene}$), 6.55 (s, 1H, H$_{thiophene}$).
13C NMR (75 MHz, CDCl3) δ = 14.1, 14.2, 15.2 (2C), 39.8, 40.9, 53.7 (2C), 62.7, 66.5 (2C), 124.3, 126.3, 128.4, 132.3, 135.2, 135.8, 136.7, 137.1, 137.2, 167.1, 206.3.
HRMS (ESI-TOF) m/z [M + H]+ calcd for C22H27NO2S2 402.1556, found 402.1552.

2,3-Bis(2,5-dimethylthiophen-3-yl)-4-methoxy-4-methylcyclopent-2-enone (9a).
To a solution of diarylethene 1 (0.30 mmol, 100 mg) in methanol (2 mL) p-toluenesulfonic acid monohydrate (0.33 mmol, 63 mg) was added. The resulting mixture was refluxed for 2 h, poured into water (100 mL) and extracted with ethyl acetate (2 × 50 mL). The combined organic phases were washed with 5% NaHCO3 (100 mL) and brine (100 mL), dried over MgSO4, and evaporated in vacuum. The residue was purified by recrystallization from ethanol.

Colorless crystals; 99% yield (103 mg), mp 123-125 °C (ethanol).

1H NMR (300 MHz, CDCl3) δ = 1.41 (s, 3H, CH3), 1.69 (s, 3H, CH3), 1.88 (s, 3H, CH3), 2.37 (s, 3H, CH3), 2.44 (s, 3H, CH3), 2.52 (d, J = 18.8 Hz, 1H, ½CH2), 2.88 (d, J = 18.8 Hz, 1H, ½CH2), 3.29 (s, 3H, OCH3), 6.48 (s, 1H, Hthiophene), 6.88 (s, 1H, Hthiophene).

13C NMR (75 MHz, CDCl3) δ = 14.4, 14.5, 15.2 (2C), 25.7, 45.4, 50.8, 81.5, 125.0, 126.4, 128.1, 130.7, 135.9, 136.0, 136.6, 137.6, 138.1, 164.1, 204.0.
HRMS (ESI-TOF) m/z [M + H]+ calcd for C19H22O2S2 347.1134, found 347.1129.

2,3-Bis(2,5-dimethylthiophen-3-yl)-4-(hexadecyloxy)-4-methylcyclopent-2-enone (9b).
To a solution of diarylethene 1 (0.30 mmol, 100 mg) in molten cetyl alcohol (2 g) p-toluenesulfonic acid monohydrate (0.33 mmol, 63 mg) was added. The resulting solution was heated at 80 °C for 2 h, poured into water (100 mL) and extracted with ethyl acetate (2 × 50 mL). The combined organic phases were washed with 5% NaHCO3 (100 mL) and brine (100 mL), dried over MgSO4, and evaporated in vacuum. The residue was purified by column chromatography by eluting with petroleum ester/ethyl acetate (15:1).

Yellow amorphous powder; 84% yield (141 mg).

1H NMR (300 MHz, CDCl3) δ = 0.90 (t, J = 6.4 Hz, 3H, CH3), 1.23-1.34 (m, 26H, (CH3)13), 1.43 (s, 3H, CH3), 1.59-1.65 (m, 2H, CH2), 1.69 (s, 3H, CH3), 1.88 (s, 3H, CH3), 2.38 (s, 3H, CH3), 2.45 (s, 3H, CH3), 2.53 (d, J = 18.6 Hz, 1H, ½CH2), 2.86 (d, J = 18.6 Hz, 1H, ½CH2), 3.33 (t, J = 6.6 Hz, 3H, CH3), 6.49 (s, 1H, Hthiophene), 6.91 (s, 1H, Hthiophene).

13C NMR (75 MHz, CDCl3) δ = 14.1, 14.4, 14.5, 15.2 (2C), 22.7, 25.9, 26.2, 29.3, 29.5, 29.6, 29.7 (7C), 30.2, 31.9, 46.3, 63.3, 81.0, 125.2, 126.4, 128.2, 131.0, 135.8, 136.0, 136.3, 137.5, 137.7, 164.9, 204.2.
HRMS (ESI-TOF) m/z [M + H]+ calcd for C34H52O2S2 557.3481, found 557.3478.
5-Bromo-2,3-bis(2,5-dimethylthiophen-3-yl)-4-methoxy-4-methylcyclopent-2-enone (10).

The mixture of diarylethene 9a (100 mg, 0.29 mmol) and CuBr₂ (390 mg, 1.74 mmol) in methanol (7 mL) was heated to reflux until completion of the reaction (TLC control). The resulting mixture was poured into water (100 mL) and extracted with dichloromethane (3 × 50 mL). The combined organic phases were washed with water (3 × 40 mL) and evaporated in vacuum. The residue was purified by column chromatography eluting by petroleum ester/ethyl acetate 20:1.

Brown powder; 61% yield (75 mg); mp 100-102 °C.

1H NMR (300 MHz, CDCl₃) δ = 1.57 (s, 3H, CH₃), 1.72 (s, 3H, CH₃), 1.94 (s, 3H, CH₃), 2.35 (s, 3H, CH₃), 2.45 (s, 3H, CH₃), 3.35 (s, 3H, OCH₃), 4.86 (s, 1H, CH), 6.43 (s, 1H, Hthiophene), 6.86 (s, 1H, Hthiophene).

13C NMR (75 MHz, CDCl₃) δ = 14.3, 14.4, 15.1, 15.2, 23.6, 51.5, 54.0, 83.4, 125.2, 126.2, 127.3, 130.0, 135.4, 136.0, 136.6, 138.4, 163.5, 196.6.

HRMS (ESI-TOF) m/z [M + H]^+ calcd for C₁₉H₂₁₇₉BrO₂S₂ 425.0239, found 425.0249; calcd for C₁₉H₂₁₁₈₁BrO₂S₂ 427.0219, found 427.0230.

4-(2,4-Dimethoxyphenyl)-2,3-bis(2,5-dimethylthiophen-3-yl)-4-methylcyclopent-2-enone (11a).

To a solution of 1,3-dimethoxybenzene (207 mg, 1.50 mmol) in trifluoroacetic acid (3 mL) diarylethene 1 (100 mg, 0.30 mmol) was added portionwise. The resulting mixture was stirred for 0.5 h and evaporated in vacuum. The residue was dissolved in dichloromethane (50 mL), washed by 5% water solution of NaHCO₃ (100 mL) and water (100 mL), dried with dry MgSO₄, and evaporated in vacuum. The residue was purified by column chromatography eluting by petroleum ether /ethyl acetate (5:1).

Colorless crystals; 80% yield (mg); mp 162-164 °C.

1H NMR (300 MHz, CDCl₃) δ = 1.53 (s, 3H, CH₃), 1.72 (s, 3H, CH₃), 1.83 (s, 3H, CH₃), 2.20 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 2.55 (d, J = 18.3 Hz, 1H, ½CH₂), 3.10 (d, J = 18.3 Hz, 1H, ½CH₂), 3.69 (s, 3H, OCH₃), 3.86 (s, 3H, OCH₃), 5.51 (s, 1H, Hthiophene), 6.45-6.55 (m, 3H, Harom + Hthiophene), 7.19 (d, J = 9.3 Hz, 1H, Harom).

13C NMR (75 MHz, CDCl₃) δ = 14.0 (2C), 15.1, 15.2, 27.3, 47.1, 51.5, 54.7, 55.4, 99.0, 103.7, 124.1, 124.3, 126.5, 128.7, 129.1, 132.1, 134.9, 135.1, 135.3, 135.9, 136.0, 158.9, 160.2, 171.0, 207.3.

HRMS (ESI-TOF) m/z [M + H]^+ calcd for C₂₆H₂₆O₃S₂ 453.1553, found 453.1543.
2,3,4-Tris(2,5-dimethylthiophen-3-yl)-4-methylcyclopent-2-enone (11b).

To a cooled (5 °C) solution of 2,5-dimethylthiophene (168 mg, 1.50 mmol) in trifluoroacetic acid (1 mL) diarylethene I (50 mg, 0.15 mmol) was added portionwise. The resulting mixture was stirred for 0.5 h and evaporated in vacuum. The residue was dissolved in dichloromethane (50 mL), washed by 5% water solution of NaHCO₃ (100 mL) and water (100 mL), dried with dry MgSO₄, and evaporated in vacuum. The residue was purified by column chromatography eluting by petroleum ether /ethyl acetate (40:1).

Light brown powder, 58% yield (37 mg).

\[ \text{H NMR (300 MHz, CDCl}_3) \delta = 1.55 \text{ (s, 3H, CH}_3), 1.72 \text{ (s, 3H, CH}_3), 1.94 \text{ (s, 3H, CH}_3), 2.28 \text{ (s, 3H, CH}_3), 2.32 \text{ (s, 3H, CH}_3), 2.36 \text{ (s, 3H, CH}_3), 2.41 \text{ (s, 3H, CH}_3), 2.71 \text{ (d, } J = 19.1 \text{ Hz, 1H, } \frac{1}{2}\text{CH}_2), 3.08 \text{ (d, } J = 19.1 \text{ Hz, 1H, } \frac{1}{2}\text{CH}_2), 5.66 \text{ (s, 1H, H}_{\text{thiophene}}), 6.42 \text{ (s, 1H, H}_{\text{thiophene}}), 6.59 \text{ (s, 1H, H}_{\text{thiophene}}). \]

\[ \text{C NMR (75 MHz, CDCl}_3) \delta = 14.0, 14.5, 14.6, 15.1, 15.2 (2C), 28.3, 47.1, 52.4, 124.2, 126.5, 127.1, 128.2, 131.6, 131.8, 134.4, 135.4, 135.6, 135.9 (2C), 136.8, 138.8, 171.5, 206.5. \]

HRMS (ESI-TOF) \( m/z \) [M + H]+ calcd for C₂₄H₂₆OS₃ 427.1219, found 427.1227.

2,3-Bis(2,5-dimethylthiophen-3-yl)-4-methylcyclopent-2-enone (12).

To a solution of diarylethene I (200 mg, 0.60 mmol) in abs. dichloromethane (2 mL) under inert atmosphere (argon) a solutions of triethylsilane (0.19 mL, 1.2 mmol) in abs. dichloromethane (2 mL) and triflic acid (60 µL, 0.66 mmol) in abs. dichloromethane (2 mL) were added dropwise simultaneously. The resulting mixture was refluxed until completion of the reaction (TLC control). The mixture was poured into 5% water solution of NaHCO₃ (100 mL) and extracted with dichloromethane (2 x 30 mL). The combined organic phases were washed with water (100 ml), dried with dry MgSO₄, and evaporated in vacuum. The residue was purified by flash chromatography by petroleum ether (100 ml) -> petroleum ether /ethyl acetate (3:1).

Yellow powder; 85% yield (162 mg); mp 96-98 °C.

\[ \text{H NMR (300 MHz, CDCl}_3) \delta = 1.12 \text{ (d, } J = 7.1 \text{ Hz, 3H, CH}_3), 1.84 \text{ (s, 3H, CH}_3), 1.88 \text{ (s, 3H, CH}_3), 2.23 \text{ (dd, } J = 18.8, 2.1 \text{ Hz, 1H, } \frac{1}{2}\text{CH}_2), 2.38 \text{ (s, 3H, CH}_3), 2.42 \text{ (s, 3H, CH}_3), 2.90 \text{ (dd, } J = 18.8, 6.7 \text{ Hz, 1H, } \frac{1}{2}\text{CH}_2), 3.24-3.37 \text{ (m, 1H, CH}, 6.45 \text{ (s, 1H, H}_{\text{thiophene}}), 6.52 \text{ (s, 1H, H}_{\text{thiophene}}). \]

\[ \text{C NMR (75 MHz, CDCl}_3) \delta = 14.1 \text{ (2C), 15.1, 15.2, 20.1, 36.6, 43.5, 124.5, 126.4, 128.6, 132.6, 135.0, 135.6, 135.9, 136.6, 136.8, 171.0, 206.8. } \]

HRMS (ESI-TOF) \( m/z \) [M + H]+ calcd for C₁₈H₂₆OS₂ 317.1028, found 317.1027.
2,3-Bis(2,5-dimethylthiophen-3-yl)-4-methylcyclopent-2-enone oxime (13).

A mixture of diarylethene 12 (170 mg, 0.54 mmol), hydroxylamine hydrochloride (151 mg, 2.15 mmol) and anhydrous sodium acetate (221 mg, 2.69 mmol) in ethanol (5 mL) was refluxed for 5 h, poured into water (100 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water (50 mL) and evaporated in vacuum. The residue was purified by column chromatography eluting by petroleum ester/ethyl acetate 10:1.

Yellow powder; 92% yield (178 mg); mp 147-149 °C.

1H NMR (300 MHz, CDCl3) δ = 1.07 (d, J = 6.6 Hz, 3H, CH3), 1.85 (s, 3H, CH3), 1.87 (s, 3H, CH3), 2.38 (s, 6H, CH3), 2.39-2.50 (m, 1H, ½CH2), 3.11-3.30 (m, 2H, CH+½CH2), 6.41 (s, 1H, Hthiophene), 6.51 (s, 1H, Hthiophene).

13C NMR (75 MHz, CDCl3) δ = 14.0 (2C), 15.1, 15.2, 20.4, 33.6, 39.8, 125.2, 126.7, 129.6, 130.8, 132.8, 134.5, 134.8, 135.4, 135.8, 155.9, 167.1.

HRMS (ESI-TOF) m/z [M + H]+ calcd for C18H21NOS2 332.1137, found 332.1135.

2,3-Bis(2,5-dimethylthiophen-3-yl)-4-methylcyclopent-2-enone O-methacryloyl oxime (14).

To a cooled (10 °C) mixture of DCC (166 mg, 0.80 mmol) and DMAP (98 mg, 0.80 mmol) in abs. dichloromethane (2 mL) a solution of methacrylic acid (69 mg, 0.80 mmol) in abs. dichloromethane (2 mL), were added. The resulting mixture was stirred for 0.5 h and solution of diarylethene 13 (133 mg, 0.40 mmol) in abs. dichloromethane (2 mL) was added. A solution was stirred for 3 h at room temperature, poured into water (100 mL) and extracted with dichloromethane (3 × 30 mL). The combined organic phases were washed with water (100 mL) and evaporated in vacuum. The residue was purified by column chromatography eluting by petroleum ester/ethyl acetate 20:1.

Light red amorphous powder.

1H NMR (300 MHz, CDCl3) δ = 1.07 (d, J = 6.3 Hz, 3H, CH3), 1.84 (s, 3H, CH3), 1.93 (s, 3H, CH3), 2.03 (s, 3H, CH3), 2.36 (s, 3H, CH3), 2.39 (s, 3H, CH3), 2.51 (dd, J = 21.2, 5.2 Hz, 1H, ½CH2), 3.21-3.38 (m, 2H, CH+½CH2), 5.62 (s, 1H, ½=CH2), 6.18 (s, 1H, ½=CH2), 6.43 (s, 1H, Hthiophene), 6.59 (s, 1H, Hthiophene).

13C NMR (75 MHz, CDCl3) δ = 14.0, 14.3, 15.1, 15.2, 18.5, 20.2, 35.1, 39.7, 124.9, 125.5, 126.9, 128.8, 130.3, 132.5, 135.2 (2C), 135.6, 135.8, 136.2, 159.9, 164.8, 174.1.

HRMS (ESI-TOF) m/z [M + H]+ calcd for C22H25NO2S2 400.1399, found 400.1388.
2,3-Bis(2,5-dimethylthiophen-3-yl)-5-(hydroxyimino)-4-methylcyclopent-2-enone (15).

To a cooled (10 °C) solution of diarylethene 12 (100 mg, 0.32 mmol) and freshly prepared n-butyl nitrite (50 mg, 0.48 mmol) in dioxane (2 mL), conc. hydrochloric acid (50 μL) was added and the 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). The combined organic phases were washed with water (50 mL), dried with dry MgSO₄ and evaporated in vacuum. The residue was purified by column chromatography eluting by petroleum ester/ethyl acetate 6:1 -> 2:1.

Green powder; 59% yield (64 mg); mp 71-73 °C.

¹H NMR (300 MHz, CDCl₃) δ = 1.34 (d, J = 7.0 Hz, 3H, CH₃), 1.88 (s, 3H, CH₃), 1.90 (s, 3H, CH₃), 2.39 (s, 3H, CH₃), 2.42 (s, 3H, CH₃), 3.96-4.08 (m, 1H, CH), 6.53 (s, 2H, Hthiophene).

¹³C NMR (75 MHz, CDCl₃) δ = 14.2, 14.4, 15.1, 15.2, 15.3, 39.6, 124.3, 125.9, 126.3, 128.0, 131.3, 135.6, 136.0, 137.1, 137.3, 138.8, 164.9, 190.2.

HRMS (ESI-TORF) m/z [M + H]^+ calcd for C₁₈H₁₉NO₂S₂ 346.0930, found 346.0930.

5-Bromo-2,3-bis(2,5-dimethylthiophen-3-yl)-4-methylcyclopent-2-enone (16).

The mixture of diarylethene 12 (100 mg, 0.32 mmol) and CuBr₂ (287 mg, 1.28 mmol) in methanol (5 mL) was heated to reflux for 1 h. The resulting mixture was poured into water (100 mL) and extracted with dichloromethane (3 × 50 mL). The combined organic phases were washed with water (50 mL) and evaporated in vacuum. The residue was purified by column chromatography eluting by petroleum ester/ethyl acetate 15:1.

Brown powder; 35% yield (44 mg).

¹H NMR (300 MHz, CDCl₃) δ = 1.24 (d, J = 7.2 Hz, 3H, CH₃), 1.86 (s, 3H, CH₃), 1.92 (s, 3H, CH₃), 2.37 (s, 3H, CH₃), 2.42 (s, 3H, CH₃), 3.44-3.56 (m, 1H, CH), 4.18 (d, J = 2.7 Hz, 1H, CH), 6.42 (s, 1H, Hthiophene), 6.51 (s, 1H, Hthiophene).

¹³C NMR (75 MHz, CDCl₃) δ = 14.2, 14.3, 15.1, 15.2, 18.1, 48.4, 50.9, 124.4, 126.2, 127.9, 131.7, 133.6, 135.9 (2C), 137.3, 138.1, 167.3, 199.2.

HRMS (ESI-TORF) m/z [M + H]^+ calcd for C₁₈H₁₉BrO₂S₂ 395.0133, found 395.0115; calcd for C₁₈H₁₉BrO₂S₂ 397.0113, found 397.0097.
(E)-2,3-Bis(2,5-dimethylthiophen-3-yl)-4-methyl-5-(4-(piperidin-1-yl)benzylidene)cyclopent-2-enone (17).

The mixture of diarylethene 12 (100 mg, 0.32 mmol) and 4-piperidin-1-ylbenzaldehyde (121 mg, 0.64 mmol) in mixture of ethanol (2 mL) and 10%-solution of NaOH in water (1 mL) was refluxed for 3 h. The resulting solution was poured into water (100 mL), extracted with ethyl acetate (3 × 30 mL) and evaporated in vacuum. The product was isolated by column chromatography eluting with petroleum ester/ethyl acetate (14:1).

Yellow powder; 44% yield (68 mg); mp 172-174 °C (ethanol).

$^1$H NMR (300 MHz, CDCl$_3$) δ = 1.19 (d, $J = 6.8$ Hz, 3H, CH$_3$), 1.57-1.80 (m, 6H, (CH$_2$)$_3$), 1.86 (s, 3H, CH$_3$), 1.94 (s, 3H, CH$_3$), 2.40 (s, 3H, CH$_3$), 2.45 (s, 3H, CH$_3$), 3.26-3.41 (m, 4H, CH$_2$), 4.10-4.25 (m 1H, CH), 6.58 (s, 1H, H$_{thiophene}$), 6.64 (s, 1H, H$_{thiophene}$), 6.86-7.07 (m, 2H, H$_{arom}$), 7.46 (s, 1H, CH), 7.54 (d, $J = 8.2$ Hz, 2H, H$_{arom}$).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ = 14.2 (2C), 15.2 (2C), 17.0, 24.2, 25.4 (2C), 40.7 (2C), 49.3, 114.9, 124.7, 126.7 (2C), 129.4, 131.6 (2C), 132.5, 132.6 (3C), 134.9, 135.4, 135.5, 136.6, 136.7, 136.9, 164.5, 194.7.

HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for C$_{30}$H$_{33}$NOS$_2$ 488.2076, found 488.2081.
III. Comparison of photochromic properties of diarylenes V and 1

Figure S1. Absorption spectra (acetonitrile, C = 6·10⁻⁵ M) of diarylenes 1 and V during irradiation by UV light (365 nm).
### IV. 2D NMR data

#### IV.1. Diarylethene 1

![Diagram of Diarylethene 1]

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**Table S1.** Full assignment for diarylethene 1.
\[ ^1{\text{H}}-^{13}{\text{C}} \] HSQC spectrum

\[ ^1{\text{H}}-^1{\text{H}} \] COSY spectrum
\(^{1}H-{ }^{1}H\) NOESY spectra
$^{1}H-^{13}C$ HMBC spectrum
$\{^1H-^{13}C\}$ HMBC spectra
$\{^1\text{H} - ^{13}\text{C}\} \text{ HMBC spectra}$
### IV.2. Diarylethene 8

The sample contains AcOH impurities (2.09 ppm in $^1$H NMR, 20.8 and 175.0 ppm in $^{13}$C NMR)

#### Table S2. Full assignment for diarylethene 8.

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The sample contains AcOH impurities (2.09 ppm in $^1$H NMR, 20.8 and 175.0 ppm in $^{13}$C NMR)
\{^1\text{H}^{13}\text{C}\} \text{ HSQC spectra}
{^1H−^1H} COSY spectrum
\{(^{1}\text{H}^{1}\text{H})\} \text{ NOESY spectra}
$\{^1\text{H}^{-13}\text{C}\}$ HMBC spectra
\{^{1}H-^{13}C\} HMBC spectra
{$^1$H–$^{13}$C} HMBC spectra
V. Copies of NMR spectra

$^1$H NMR spectrum, compound 1 (CDCl$_3$)

$^1$H NMR spectrum, compound 1 (DMSO-d$_6$)
$^{13}$C DEPT spectrum, compound 1 (CDCl$_3$)
$^1$H NMR spectrum, compound 5 (CDCl$_3$)

$^{13}$C NMR spectrum, compound 5 (CDCl$_3$)
$^1$H NMR spectrum, compound 6 (CDCl$_3$)

$^{13}$C NMR spectrum, compound 6 (CDCl$_3$)
$^1$H NMR spectrum, compound 7 (CDCl$_3$)

$^{13}$C NMR spectrum, compound 7 (CDCl$_3$)
$^1$H NMR spectrum, compound 8 (CDCl$_3$)

$^{13}$C NMR spectrum, compound 7 (CDCl$_3$)
$^1$H NMR spectrum, compound 9a (CDCl$_3$)

$^{13}$C NMR spectrum, compound 9a (CDCl$_3$)
$^1$H NMR spectrum, compound 9b (CDCl$_3$)

$^{13}$C NMR spectrum, compound 9b (CDCl$_3$)
$^1$H NMR spectrum, compound 10 (CDCl$_3$)

$^{13}$C NMR spectrum, compound 10 (CDCl$_3$)
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$^1$H NMR spectrum, compound 13 (CDCl$_3$)

$^{13}$C NMR spectrum, compound 13 (CDCl$_3$)
$^1$H NMR spectrum, compound 14 (CDCl$_3$)

$^{13}$C NMR spectrum, compound 14 (CDCl$_3$)
$^1$H NMR spectrum, compound 15 (CDCl$_3$)

$^{13}$C NMR spectrum, compound 15 (CDCl$_3$)
\(^1\)H NMR spectrum, compound \(16\) (CDCl\(_3\))

\(^{13}\)C NMR spectrum, compound \(16\) (CDCl\(_3\))
$^1$H NMR spectrum, compound 17 (CDCl$_3$)

$^{13}$C NMR spectrum, compound 17 (CDCl$_3$)
VI. Copies of HRMS spectra

Compound 1

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![HRMS Spectrum](image)

**Bruker Compass DataAnalysis 4.0**

printed: 11.02.2016 17:05:46 Page 1 of 1
Compound 5

Display Report

Analysis Info
Analysis Name: D:\Data\Kolotyrkina\2017\L'vov\0419001.d
Method: tune_wide.m
Sample Name: /SNMR R-704
Comment: C18H18O5S mH 315.0871 calibrant added

Acquisition Parameter
Source Type: ESI
Ion Polarity: Positive
Focus: Not active
Scan Begin: 50 m/z
Scan End: 3000 m/z
Set Capillary: 4500 V
Set End Plate Offset: -500 V
Set Nebulizer: 0.4 Bar
Set Dry Heater: 180 °C
Set Dry Gas: 4.0 l/min
Set Divert Valve: Waste

Bruker Compass DataAnalysis 4.0  
printed: 19.04.2017 10:17:54  
Page 1 of 1
Compound 6
Compound 8
Compound 9a

Display Report

Analysis Info
Analysis Name: D:\Data\Kolotyrkina2017\L'vov/0419006.d
Method: tune_wide.m
Sample Name: /SNMR MN-106b-A
Comment: C19H22O2S2 mH 347.1133 calibrant added

Acquisition Parameter
Source Type: ESI
Ion Polarity: Positive
Set Nebulizer: 0.4 Bar
Focus: Not active
Set Capillary: 4500 V
Set Dry Heater: 180 °C
Scan Begin: 50 m/z
Set End Plate Offset: -500 V
Scan End: 3000 m/z
Set Divert Valve: Waste

Bruker Compass DataAnalysis 4.0 printed: 19.04.2017 11:01:22 Page 1 of 1
Compound 9b
Compound 10
Compound 11a
Compound 11b
Compound 12
Compound 13
Compound 14
**Compound 15**

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**Display Report**

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**Acquisition Parameter**

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<td>Set Nebulizer</td>
<td>0.4 Bar</td>
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<td>Set Dry Gas</td>
<td>2.0 bar</td>
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<td>Set Divert Valve</td>
<td>Waste</td>
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**Chemical Structure**

![Chemical Structure Image]

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Bruker Compass DataAnalysis 4.0 printed: 23.06.2017 14:31:22 Page 1 of 1

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S60
Compound 16
**Compound 17**

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**Acquisition Parameter**

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<tr>
<td>Scan End</td>
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</table>

**Ion Polarity**

| Positive Set Nebulizer 0.4 Bar |
| Set Dry Heater 180 °C |
| Set Divert Valve Waste |

**Display Report**

[Chemical structure image of Compound 17]

Bruker Compass DataAnalysis 4.0  
printed: 2016.06.17 15:30:28  
Page 1 of 1