Supplementary data

FACILE SYNTHESIS OF PHOTOACTIVE DIARYL(HETARYL)CYCLOPENTENES BY IONIC HYDROGENATION

Andrey G. Lvov,¹ Ekaterina Yu. Bulich,² Anatoly V. Metelitsa,³ Valerii Z. Shirinian¹*

¹N.D. Zelinsky Institute of Organic Chemistry RAS, 47 Leninsky prosp., 119991 Moscow,

Russian Federation, e-mail: <u>shir@ioc.ac.ru</u>

² Mendeleev University of Chemical Technology of Russia, Miusskaya Sq., 9, Moscow, 125047,

Russian Federation

³ Institute of Physical and Organic Chemistry, Southern Federal University, 194/2 Stachka

Avenue, Rostov on Don 344090, Russian Federation

N⁰	Table of the content	Page
1	Experimental section	S2
2	Copies of ¹ H and ¹³ C NMR spectra of diarylethenes 3 and 4	S9
3	References	S23

1. EXPERIMENTAL SECTION

General. Proton nuclear magnetic resonance spectra (¹H NMR) and carbon nuclear magnetic resonance spectra (¹³C NMR) were recorded in deuterated solvents on a spectrometers working at 300 MHz for ¹H, 75 MHz for ¹³C. Both ¹H and ¹³C NMR chemical shifts are referenced relative to the solvents residual signals (CHCl₃: δ 7.27 for ¹H NMR and δ 77.16 for ¹³C 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; br, broad), coupling constant in hertz (Hz), integration, and assignment. Melting points (Mp) were recorded using an apparatus and not corrected. Mass spectra were obtained on a mass spectrometer (70 eV) with direct sample injection into the ion source. 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 F254 plates.

Photochemical studies. UV–Vis spectra were recorded in 1.0 cm quartz cuvettes. The experimental measurements were performed at 293 K in the presence of air in acetonitrile solution. Photocoloration and photobleaching reactions were carried out using high-pressure mercury lamp as the exciting light source. The required wavelengths (313 and 517 nm) were isolated by the use of the appropriate filters.

Synthesis of diarylethenes 3

New diarylcyclopentenones **3b**, **3d**, **3e**, **3h**, **3i** were prepared according method [S1] from corresponding ketoesters and bromoketones. Compound **3d** was used without purification. Diarylethenes **3a** [S2], **3c** [S3], **3f** [S4], **3g** [S4], **3j** [S1], **3h** [S3] and **4a** [S2] were described previously.



3-(2-Methylimidazo[1,2-*a***]pyridin-3-yl)-2-phenylcyclopent-2-en-1-one** (**3b**). Yield 52%, yellow crystals, m.p. 145-146 °C. ¹H NMR (300 MHz,

Solution CDCl₃): δ 2.58 (s, 3H, CH₃), 2.72-2.88 (m, 2H, CH₂), 3.15-3.27 (m, 2H, CH₂), 6.44 (t, J = 6.8 Hz, 1H, H^{imidazopyridine}), 7.05-7.33 (m, 7H, H^{arom}), 7.53 (d, J = 9.0 Hz, 1H, H^{imidazopyridine}). ¹³C NMR (75 MHz, CDCl₃): 15.6, 29.8, 35.2, 112.0, 116.5, 117.8, 125.2, 125.6, 127.9, 128.3, 128.5, 131.9, 137.0, 145.0, 145.9, 156.2, 206.1. MS, m/z (%): 288 (100, [M]⁺), 273 (10, [M-CH₃]⁺). HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₁₉H₁₇N₂O: 289.1335; found: 289.1343.

2-(2,5-Dimethylthiophen-3-yl)-3-(2-antracen-9-yl-5-methyl-1,3-oxazol-4-yl)cyclopent-2-en-



1-one (3d). Yield 15% (NMR data). ¹H NMR (300 MHz, CDCl₃): δ 1.98 (s, 3H, CH₃), 2.22 (s, 3H, CH₃), 2.46 (s, 3H, CH₃), 2.68-2.75 (m, 2H, CH₂), 3.22-3.29 (m, 2H, CH₂), 6.69 (s, 1H, H^{thiophene}), 7.47-7.58 (m, 4H, H^{arom}), 7.93-8.11 (m, 2H, H^{arom}), 8.62 (s, 1H, H^{arom}).

¹³C NMR (75 MHz, CDCl₃): 11.2, 14.4, 15.3, 29.4, 34.6, 121.1, 125.3, 125.5, 126.8, 127.2, 127.3, 128.7, 129.0, 130.4, 131.0, 131.1, 131.3, 131.4, 133.1, 134.9, 135.7, 136.5, 149.7, 161.2, 207.8. MS, *m*/*z* (%): 449 (75, [M]⁺), 434 (25, [M-CH₃]⁺), 205 (100). HRMS (ESI-TOF) m/*z*: [M+H]⁺ calcd for C₂₉H₂₄NO₂S: 450.1522; found: 450.1511.

2-(2,5-Dimethylthiophen-3-yl)-3-(4-methyl-2-phenyl-1,3-thiazol-5-yl)cyclopent-2-en-1-one



(3e). Yield 32%, light red crystalls, m.p. 142-144 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.04 (s, 3H, CH₃), 2.33 (s, 3H, CH₃), 2.42 (s, 3H, CH₃), 2.65-2.74 (m, 2H, CH₂), 3.07-3.20 (m, 2H, CH₂), 6.45 (s, 1H, H^{thiophene}), 7.37-7.50 (m, 3H, H^{arom}), 7.83-7.94 (m, 2H, H^{arom}). ¹³C NMR

(75 MHz, CDCl₃): $\delta = 14.2$, 15.3, 18.0, 31.5, 34.7, 126.1, 126.5, 128.0, 128.3, 129.0, 130.5, 133.0, 136.1, 136.8, 137.0, 154.4, 159.9, 168.7, 206.5. MS (EI, 70 eV): m/z (%) = 365 (100, [M]⁺), 350 (60, [M-CH₃]⁺). HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₁H₂₀NOS₂: 366.0981; found: 366.0971.

2-(2,5-Dimethylthiophen-3-yl)-3-(6-methylimidazo[2,1-b][1,3]thiazol-5-yl)cyclopent-2-en-1-



one (3h). Yield 20%, yellow powder, m.p. 157-158 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 1.72$ (s, 3H, CH₃), 2.36 (s, 3H, CH₃), 2.50 (s, 3H, CH₃), 2.58-2.75 (m, 2H, CH₂), 3.06-3.23 (m, 2H, CH₂), 6.44 (d, J = 4.2 Hz, 1H, H^{imidazothiazole}), 6.53 (d, J = 4.2 Hz, 1H, H^{imidazothiazole}), 6.61 (s,

1H, H^{thiophene}). ¹³C NMR (75 MHz, CDCl₃): δ = 13.8, 15.2, 16.5, 29.7, 34.6, 111.1, 119.8, 126.2, 128.9, 132.1, 136.0, 137.2, 147.8, 151.5, 156.0, 206.4. MS (EI, 70 eV): m/z (%) = 328 (100, [M]⁺), 313 (15, [M-CH₃]⁺). HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₁₇H₁₇N₂OS₂: 329.0777; found: 329.0775.

2-(2,5-Dimethylthiophen-3-yl)-3-(2-methylimidazo[1,2-a]pyridin-3-yl)cyclopent-2-en-1-one



(3i). Yield 34%, yellow powder, m.p. 161-163 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.54 (s, 3H, CH₃), 2.30 (s, 3H, CH₃), 2.55 (s, 3H, CH₃), 2.67-2.77 (m, 2H, CH₂), 3.12-3.26 (m, 2H, CH₂), 6.45-6.57 (m, 2H,

H^{thiophene} + H^{imidazopyridine}), 7.15 (m, 1H, H^{imidazopyridine}), 7.30 (d, J = 6.9 Hz, 1H, H^{imidazopyridine}), 7.50 (d, J = 8.9 Hz, 1H, H^{imidazopyridine}). ¹³C NMR (75 MHz, CDCl₃): $\delta = 13.7$, 15.1, 15.8, 29.9, 34.8, 111.8, 116.5, 118.4, 125.2, 125.5, 128.9, 134.2, 136.0, 136.9, 145.5, 145.9, 156.0, 206.5.

MS (EI, 70 eV): m/z (%) = 322 (100, [M]⁺), 307 (35, [M-CH₃]⁺). HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₁₉H₁₉N₂OS: 323.1213; found: 323.1211.

Di(het)arylcyclopentenes 4 (general). To a solution of initial diarylethene **3** (0.6 mmol) in abs. dichloromethane (3 ml) under inert atmosphere (argon) the triethylsilane (210 mg, 1.8 mmol) in abs. dichloromethane (3 ml) and trifluoromethanesulfonic acid (180 mg, 1.2 mmol) in abs. dichloromethane (3 ml) were added dropwise simultaneously. Resulting emulsion was mixed at ambient temperature (diarylethenes **3a**, **3c**, **3d**, **3e**) or refluxed (diarylethenes **3b**, **3f**, **3g**, **3h**, **3i**) until complete consumption of starting diarylcyclopentenone (monitored by TLC). Solution 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 magnesium sulfate, and evaporated in vacuum. The residue was purified by flash chromatography by petroleum ether (150 ml, for removing of silicon-containing impurities) and petroleum ether /ethyl acetate (6:1 or 4:1).



2-Methyl-3-(2-phenylcyclopent-1-en-1-yl)imidazo[1,2-*a*]**pyridine (4b).** Yield 105 mg (64%), yellow amorphous powder. ¹H NMR (300 MHz, CDCl₃): δ = 2.12-2.25 (m, 2H, CH₂), 2.32 (s, 3H, CH₃), 2.89 (t, *J* = 7.4 Hz, 2H, CH₂), 3.06 (t, *J* = 7.3 Hz, 2H, CH₂), 6.60 (t, *J* = 6.8 Hz, 1H,

H^{imidazopyridine}), 6.97-7.17 (m, 6H, H^{arom}), 7.57 (t, J = 8.3 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ = 14.1, 22.6, 36.6, 37.6, 111.5, 116.4, 118.8, 123.8, 124.0, 125.3, 126.4, 127.3, 128.3, 136.8, 140.5, 142.8, 144.4. MS (EI, 70 eV): m/z (%) = 274 (10) [M]⁺, 78 (100). HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₁₉H₁₉N₂: 275.1543; found: 275.1542.



4-[2-(2,5-Dimethylthiophen-3-yl)cyclopent-1-en-1-yl]-5-methyl-2-

phenyl-1,3-oxazole (4c). Yield 130 mg (65%), yellow crystalls, m.p. 99-103 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.80 (s, 3H, CH₃), 2.02-2.12

(m, 2H, CH₂), 2.03 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 2.78 (t, *J* = 7.4 Hz, 2H, CH₂), 2.93 (t, *J* = 7.4

Hz, 2H, CH₂), 6.48 (s, 1H, H^{thiophene}), 7.48-7.47 (m, 3H, H^{arom}), 7.97-8.04 (m, 2H, H^{arom}). ¹³C NMR (75 MHz, CDCl₃): δ = 10.6, 14.2, 15.1, 22.7, 36.8, 38.8, 126.0, 126.2, 127.7, 128.6, 129.7, 130.0, 132.0, 133.9, 135.2, 135.5, 135.8, 144.9, 159.2. MS (EI, 70 eV): m/z (%) = 335 (35) [M]⁺, 320 (30) [M-CH₃]⁺, 214 (100). HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₁H₂₂NOS: 336.1417; found: 336.1419.

4-[2-(2,5-Dimethylthiophen-3-yl)cyclopent-1-en-1-yl]-2-antracen-9-yl-5-methyl-1,3-oxazole



(4d). Yield 159 mg (61%), yellow powder, m.p. 137-138 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 1.95$ (s, 3H, CH₃), 2.05-2.17 (m, 2H, CH₂), 2.21 (s, 3H, CH₃), 2.43 (s, 3H, CH₃), 2.81 (t, J = 7.4 Hz, 2H, CH₂), 3.06 (t, J = 7.4 Hz, 2H, CH₂), 6.60 (s, 1H, H^{thiophene}), 7.41-7.52 (m, 4H, H^{arom}), 8.00-8.10 (m, 4H, H^{arom}), 8.58 (s, 1H, H^{arom}).

¹³C NMR (75 MHz, CDCl₃): $\delta = 10.7$, 14.4, 15.2, 22.8, 37.0, 39.0, 122.2, 125.3, 125.7, 126.2, 126.7, 126.8, 128.5, 129.8, 130.3, 131.2, 131.3, 131.7, 131.8, 133.9, 135.4, 135.8, 135.9, 145.7, 157.7. MS (EI, 70 eV): m/z (%) = 435 (100) [M]⁺, 420 (60) [M-CH₃]⁺. HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₉H₂₆NOS: 436.1730; found: 436.1720.



5-[2-(2,5-Dimethylthiophen-3-yl)cyclopent-1-en-1-yl]-4-methyl-2phenyl-1,3-thiazole (4e). Yield 126 mg (60%), yellow crystalls, m.p. 130-131 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.00 (s, 3H, CH₃), 2.03-2.13 (m, 2H, CH₂), 2.10 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 2.75-2.95 (m,

4H, CH₂), 6.46 (s, 1H, H^{arom}), 7.35-7.46 (m, 3H, H^{arom}), 7.80-7.92 (m, 2H, H^{arom}). ¹³C NMR (75 MHz, CDCl₃): δ = 14.2, 15.2, 16.5, 22.9, 38.9, 39.5, 125.7, 126.2, 128.8, 129.1, 129.5, 129.8, 132.9, 133.8, 134.6, 135.9, 138.0, 149.8, 164.8. MS (EI, 70 eV): m/z (%) = 351 (100) [M]⁺. HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₁H₂₂NS₂: 352.1188; found: 352.1179.

4-[2-(2,5-Dimethylthiophen-3-yl)cyclopent-1-en-1-yl]-1,5-dimethyl-2-phenyl-1H-imidazole



(4f). Yield 104 mg (50%), yellow amorphous powder. ¹H NMR (300 MHz, CDCl₃): δ = 1.65 (s, 3H, CH₃), 1.95 (s, 3H, CH₃), 1.97-2.09 (m, 2H, CH₂), 2.37 (s, 3H, CH₃), 2.71-2.83 (m, 2H, CH₂), 2.90-3.01 (m, 2H, CH₂), 3.48 (s, 3H, NCH₃), 6.49 (s, 1H, H^{arom}), 7.34-7.65 (m, 5H, H^{arom}).

¹³C NMR (75 MHz, CDCl₃): $\delta = 9.4$, 14.3, 15.1, 22.8, 31.8, 37.6, 38.8, 125.8, 126.5, 128.2, 128.4, 128.9, 131.2, 131.6, 133.0, 133.4, 134.8, 135.4, 136.1, 146.5. MS (EI, 70 eV): m/z (%) = 348 (100) [M]⁺. HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₂H₂₄N₂S: 349.1733; found: 349.1179.



4-[2-(2,5-Dimethylthiophen-3-yl)cyclopent-1-en-1-yl]-5-methyl-1,2diphenyl-1*H*-imidazole (4g). Yield 98 mg (40%), yellow amorphous powder. ¹H NMR (300 MHz, CDCl₃): $\delta = 1.44$ (s, 3H, CH₃), 2.03 (s, 3H, CH₃), 2.03-2.13 (m, 2H, CH₂), 2.37 (s, 3H, CH₃), 2.74-2.86 (m, 2H,

CH₂), 2.99-3.12 (m, 2H, CH₂), 6.52 (s, 1H, H^{arom}), 7.04-7.44 (m, 10H, H^{arom}). ¹³C NMR (75 MHz, CDCl₃): $\delta = 10.0, 14.3, 15.1, 22.9, 37.4, 38.8, 126.5, 127.1, 127.7, 127.8, 128.0, 128.2, 128.4, 129.4, 130.8, 131.6, 133.1, 133.8, 134.9, 135.9, 136.0, 137.7, 145.7. MS (EI, 70 eV): <math>m/z$ (%) = 410 (40) [M]⁺, 395 (100) [M-CH₃]⁺. HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₂H₂₄N₂S: 411.1889; found: 411.1879.

5-[2-(2,5-Dimethylthiophen-3-yl)cyclopent-1-en-1-yl]-6-methylimidazo[2,1-b][1,3]thiazole



(4h). Yield 107 mg (57%), light brown amorphous powder. ¹H NMR (300 MHz, CDCl₃): $\delta = 1.73$ (s, 3H, CH₃), 2.00-2.13 (m, 2H, CH₂), 2.22 (s, 3H, CH₃), 2.34 (s, 3H, CH₃), 2.74-2.94 (m, 4H, CH₂), 6.41-6.53 (m, 2H, H^{thiophene}+H^{imidazothiazole}), 6.67 (d, J = 4.4 Hz, 1H, H^{imidazothiazole}). ¹³C

NMR (75 MHz, CDCl₃): δ = 13.8, 14.4, 15.1, 23.1, 37.0, 38.2, 110.5, 118.6, 125.3, 125.5, 126.4, 133.0, 134.4, 136.2, 136.3, 141.0, 147.4. MS (EI, 70 eV): m/z (%) = 314 (100) [M]⁺. HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₁₇H₁₉N₂S₂: 315.0984; found: 315.0972.

3-[2-(2,5-Dimethylthiophen-3-yl)cyclopent-1-en-1-yl]-2-methylimidazo[1,2-a]pyridine (4g).



Yield 88 mg (48%), yellow amorphous powder. ¹H NMR (300 MHz, CDCl₃): $\delta = 1.64$ (s, 3H, CH₃), 2.07-2.18 (m, 2H, CH₂), 2.25 (s, 3H, CH₃), 2.28 (s, 3H, CH₃), 2.80-2.94 (m, 4H, CH₂), 6.39 (s, 1H, H^{thiophene}), 6.51-6.60 (m, 1H, H^{imidazopyridine}), 6.99-7.09 (m, 1H, H^{imidazopyridine}), 7.45

(d, J = 9.0 Hz, 1H, H^{imidazopyridine}), 7.56 (d, J = 6.9 Hz, 1H, H^{imidazopyridine}). ¹³C NMR (75 MHz, CDCl₃): $\delta = 13.8$, 14.3, 15.0, 23.3, 36.6, 38.1, 111.1, 116.3, 119.2, 123.2, 124.0, 125.0, 126.1, 133.0, 134.4, 135.8, 138.9, 141.1, 144.3. MS (EI, 70 eV): m/z (%) = 308 (100) [M]⁺. HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₁₉H₂₁N₂S: 309.1420; found: 309.1422.



5-Methyl-2-phenyl-4-(2-phenylcyclopent-2-en-1-yl)-1,3-oxazole (8). Yield 18 mg (10%), yellow amorphous powder. ¹H NMR (300 MHz, CDCl₃): $\delta = 2.05-2.19$ (m, 1H, ¹/₂ CH₂), 2.20 (s, 3H, CH₃), 2.48-2.80 (m, 3H, CH₂ + ¹/₂CH₂), 4.31-4.43 (s, 1H, CH), 7.12-7.46 (m, 8H, H^{arom}), 7.91-8.02

(m, 2H, H^{arom}). ¹³C NMR (75 MHz, CDCl₃): $\delta = 10.5$, 32.1, 32.6, 42.5, 126.0, 126.7, 127.1, 128.4, 128.7, 128.9, 129.5, 131.1, 135.6, 136.6, 142.4, 144.2, 159.1. MS (EI, 70 eV): m/z (%) = 301 (100) [M]⁺, 286 (95). HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₁H₂₀NO: 302.1539; found: 302.1539.

2. COPIES OF ¹H AND ¹³C NMR SPECTRA OF DIARYLETHENES 3 AND 4





2-(2,5-Dimethylthiophen-3-yl)-3-(2-antracen-9-yl-5-methyl-1,3-oxazol-4-yl)cyclopent-2-en-1-one (3d)¹

¹ NMR spectra are given for crude sample (without column chromatography)

2-(2,5-Dimethylthiophen-3-yl)-3-(4-methyl-2-phenyl-1,3-thiazol-5-yl)cyclopent-2-en-1-one

(**3e**)

2-(2,5-Dimethylthiophen-3-yl)-3-(6-methylimidazo[2,1-*b*][1,3]thiazol-5-yl)cyclopent-2-en-1one (3h)

2-(2,5-Dimethylthiophen-3-yl)-3-(2-methylimidazo[1,2-*a*]pyridin-3-yl)cyclopent-2-en-1-one (3i)

4-[2-(2,5-Dimethylthiophen-3-yl)cyclopent-1-en-1-yl]-5-methyl-2-phenyl-1,3-oxazole (4c)

 $\label{eq:2-2-2-2} 4-[2-(2,5-Dimethylthiophen-3-yl)cyclopent-1-en-1-yl]-2-antracen-9-yl-5-methyl-1, 3-oxazole and a statistical statisti$

(**4d**)

S17

4-[2-(2,5-Dimethylthiophen-3-yl)cyclopent-1-en-1-yl]-1,5-dimethyl-2-phenyl-1*H*-imidazole

(**4f**)

 $\label{eq:2-2-2-2} 4-[2-(2,5-Dimethylthiophen-3-yl) cyclopent-1-en-1-yl]-5-methyl-1,2-diphenyl-1 \\ H-imidazole$

(**4**g)

 $\label{eq:constraint} 5-[2-(2,5-Dimethylthiophen-3-yl) cyclopent-1-en-1-yl]-6-methylimidazo [2,1-b] [1,3] thiazole$

(**4h**)

5-Methyl-2-phenyl-4-(2-phenylcyclopent-2-en-1-yl)-1,3-oxazole (8)

3. REFERENCES

- S1. V. Z. Shirinian, A. A. Shimkin, D. V. Lonshakov, A. G. Lvov and M. M. Krayushkin, J. Photochem. Photobiol., A, 2012, 233, 1.
- S2. A. G. Lvov, V. Z. Shirinian, V. V Kachala, A. M. Kavun, I. V. Zavarzin, M. M. Krayushkin, Org. Lett., 2014, 16, 4532.
- S3. V. Z. Shirinian, A. G. Lvov, M. M. Krayushkin, E. D. Lubuzh and B. V. Nabatov, J. Org. Chem., 2014, **79**, 3440.
- S4. V. Z. Shirinian, A. G. Lvov, E. Yu. Bulich, A. V. Zakharov and M. M. Krayushkin, *Tetrahedron Lett.*, 2015, **56**, 5477.