

Synthesis and spectral properties of 3-(2-aryl-5-methyl-1,3-oxazol-4-yl)-2-(2,5-dimethylthiophen-3-yl)cyclopent-2-en-1-ones

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Table of contents

1. Experimental
2. UV-vis spectra of compounds **4a-e**
3. NMR signals of initial and photoinduced forms of diarylethenes **4a-e**
4. Fluorescence modulation for diarylethene **4d**
5. Copies of ¹H, ¹³C NMR spectra of compounds **4b-d**

1. Experimental

1.1. General

¹H and ¹³C NMR spectra were recorded on a Bruker AM-300 spectrometer. Mass spectra were obtained on a Kratos mass spectrometer (70 eV) with direct sample inlet 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.

UV–Vis and fluorescence spectra were recorded in 1.0 cm quartz cuvettes. The experiments were performed in acetonitrile solutions ($C = 2 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ for absorption spectra) at 293 K in the presence of air. 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. Molar extinction coefficients of the photogenerated isomers were determined as follows: a diarylethene (10 mg) was dissolved in dichloromethane (3 ml) and the solution was irradiated with UV-light (313 nm) for 30-45 minutes in 1.0 cm quartz cuvette. The obtained deeply colored solution was evaporated in dark under vacuum and the residue was used in preparation of samples for NMR and UV/Vis spectroscopy studies. Molar extinction coefficients (ϵ_c) were calculated by equation (1):

$$\varepsilon_c = \frac{D}{conv \times c_0} \quad (1)$$

where D is the absorption at band maximum of photogenerated isomer; $conv$ is the conversion of diarylethene; c_0 is the total concentration of the compound.

Quantum yields of ring-closure and ring-opening processes were calculated by equations (2) and (3), respectively:*

$$\ln \frac{D(\infty) - D(0)}{D(\infty) - D(t)} = 2.303 \times 10^3 \times I_0 \times \varepsilon_0 \times \varphi_{o-c} \times t \times \frac{c_0}{c_B(\infty)} \quad (2)$$

$$\ln \frac{D(0)}{D(t)} = 2.303 \times 10^3 \times I_0 \times \varepsilon_c \times \varphi_{c-o} \times t \quad (3)$$

where $D(\infty)$ is the absorption at band maximum of photogenerated isomer in photostationary state (PSS); $D(t)$ is the absorption at time t and $D(0)$ is the initial absorption; I_0 is the irradiation light intensity; ε_0 and ε_c are molar extinction coefficients of initial and photogenerated isomers at the irradiation wavelength, respectively; c_0 and $c_B(\infty)$ are the total concentration and the concentration of photogenerated isomer in PSS, respectively; φ_{o-c} and φ_{c-o} are cyclization and ring opening quantum yield, respectively, and $\varepsilon_0 \times c_0$ and $\varepsilon_c \times c_B(\infty)$ are lower than 0.2.

1,2-Bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene in hexane solution[†] was used as a chemical actinometer.

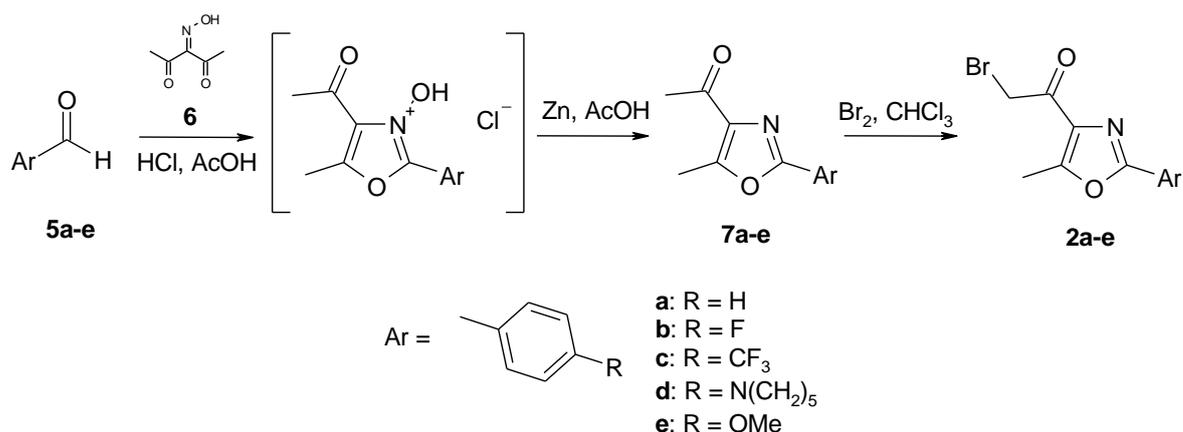
The half-lives of thermal bleaching for the diarylethenes were determined as follows. The solution of open-ring form in acetonitrile ($C \approx 2 \times 10^{-5}$ M) was irradiated with UV light ($\lambda = 313$ nm) until reaching the photostationary state and was kept in dark at 293 K. The reaction yields were periodically determined by absorption spectroscopic measurement. The thermal bleaching process was determined as a first order reaction (linearity for relationships between the logarithms of absorbance and exposal time) that is well-known fact.[‡]

* H. Nakashima and M. Irie, *Macromol. Chem. Phys.*, 1999, **200**, 683.

† K. Uchida, E. Tsuchida, Y. Aoi, S. Nakamura and M. Irie, *Chem. Lett.*, 1999, 63.

‡ D. Kitagawa, K. Sasaki and S. Kobatake, *Bull. Chem. Soc. Jpn.*, 2011, **84**, 141.

1.2. Synthesis of starting materials



Scheme S1. Synthetic route for bromo ketones **2a-e**.

The synthetic route for bromo ketones **2** is shown in Scheme S1. Oxazole **7a** was prepared according to known procedure,[§] and oxazoles **7b-e** were prepared from corresponding commercially available aldehydes and 3-(hydroxyimino)pentane-2,4-dione **6** by this method. Aldehyde **5d** was prepared from 4-fluorobenzaldehyde and piperidine as described.^{**} Bromo ketone **2a** was prepared according to known procedure,^{††} and bromo ketones **2b-e** were prepared by this method.

1-[2-(4-Fluorophenyl)-5-methyl-1,3-oxazol-4-yl]ethanone (**7b**)

Yield 60%, white solid, Mp 84-85 °C. ¹H NMR (300 MHz, CDCl₃): δ 2.59 (s, 3H, CH₃), 2.69 (s, 3H, CH₃), 7.16 (dd, *J* = 8.4, 8.4 Hz, 2H, H^{arom}), 8.04 (dd, *J* = 5.3, 8.4 Hz, 2H, H^{arom}). MS, *m/z* (%): 220 [M+H]⁺ (30), 219 [M]⁺ (60), 204 [M-CH₃]⁺ (75). Anal. Calcd for C₁₂H₁₀FNO₂: C, 65.75; H, 4.60. Found: C, 65.84; H, 4.76.

1-{5-Methyl-2-[4-(trifluoromethyl)phenyl]-1,3-oxazol-4-yl}ethanone (**7c**)

Yield 65%, white solid, Mp 81-82 °C. ¹H NMR (300 MHz, CDCl₃): δ 2.62 (s, 3H, CH₃), 2.73 (s, 3H, CH₃), 7.74 (d, *J* = 8.2 Hz, 2H, H^{arom}), 8.16 (d, *J* = 8.2 Hz, 2H, H^{arom}). MS, *m/z* (%): 270 [M+H]⁺ (15), 269 [M]⁺ (50), 254 [M-CH₃]⁺ (60). Anal. Calcd for C₁₃H₁₀F₃NO₂, %: C, 58.00; H, 3.74; N, 5.20. Found: C, 58.40; H, 4.05; N, 5.40.

1-{5-Methyl-2-[4-(piperidin-1-yl)phenyl]-1,3-oxazol-4-yl}ethanone (**7d**)

Yield 70%, yellow solid, Mp 50-51 °C. ¹H NMR (300 MHz, CDCl₃): δ 1.61-1.74 (m, 6H, (CH₂)₃), 2.59 (s, 3H, CH₃), 2.67 (s, 3H, CH₃), 3.26-3.34 (m, 4H, (CH₂)₂), 6.94 (d, *J* = 8.8 Hz,

[§] A. Allan and B. Walter, *J. Chem. Soc.*, 1968, 1397.

^{**} V. Z. Shirinian, A. A. Shimkin, D. V. Lonshakov, A. K. Mailyan, A. G. Lvov and M. M. Krayushkin, *Synthesis*, 2012, 527.

^{††} T. Sohda, K. Mizuno, Y. Momose, H. Ikeda, T. Fujita and K. Meguro, *J. Med. Chem.*, 1992, **35**, 2617.

2H, H^{arom}), 7.88 (d, $J = 8.8$ Hz, 2H, H^{arom}). MS, m/z (%): 284 [M]⁺ (100). Anal Calcd for C₁₇H₂₀N₂O₂, %: C, 71.81; H, 7.09; N, 9.85. Found, %: C, 71.91; H, 7.55; N, 9.95.

1-[2-(4-Methoxyphenyl)-5-methyl-1,3-oxazol-4-yl]ethanone (7e)

Yield 65%, white solid, Mp 92-94 °C. ¹H NMR (300 MHz, CDCl₃): δ 2.59 (s, 3H, CH₃), 2.68 (s, 3H, CH₃), 3.87 (s, 3H, OCH₃), 6.97 (d, $J = 8.8$ Hz, 2H, H^{arom}), 7.97 (d, $J = 8.8$ Hz, 2H, H^{arom}). MS, m/z (%): 231 [M]⁺ (100), 216 [M-CH₃]⁺ (40). Anal Calcd for C₁₃H₁₃NO₃, %: C, 67.52; H, 5.67; N, 6.06. Found, %: C, 67.54; H, 5.80; N, 6.04.

2-Bromo-1-[2-(4-fluorophenyl)-5-methyl-1,3-oxazol-4-yl]ethanone (2b)

Compound **2c** was prepared by a method similar to that used for **2a**.

Yield 95%, white solid, Mp 120-121 °C. ¹H NMR (300 MHz, CDCl₃): δ 2.73 (s, 3H, CH₃), 4.58 (s, 2H, CH₂), 7.17 (dd, $J = 8.6, 8.6$ Hz, 2H, H^{arom}), 8.04 (dd, $J = 5.3, 8.6$ Hz, 2H, H^{arom}). MS, m/z (%): 297, 299 [M]⁺ (10), 218 [M-Br]⁺ (100). Anal Calcd for C₁₂H₉BrFNO₂, %: C, 44.35; H, 3.04; N, 4.70. Found, %: C, 44.33; H, 3.01; N, 4.78.

2-Bromo-1-{5-methyl-2-[4-(trifluoromethyl)phenyl]-1,3-oxazol-4-yl}ethanone (2c)

Yield 98%, white solid, Mp 86-87 °C. ¹H NMR (300 MHz, CDCl₃): δ 2.76 (s, 3H, CH₃), 4.58 (s, 2H, CH₂), 7.74 (d, $J = 8.0$ Hz, 2H, H^{arom}), 8.16 (dd, $J = 8.0$ Hz, 2H, H^{arom}). MS, m/z (%): 347, 349 [M]⁺ (15), 268 [M-Br]⁺ (80), 254 [M-CH₂Br]⁺ (100). Anal Calcd for C₁₃H₉BrF₃NO₂, %: C, 44.85; H, 2.61; N, 4.02. Found, %: C, 44.88; H, 2.58; N, 4.12.

2-Bromo-1-{5-methyl-2-[4-(piperidin-1-yl)phenyl]-1,3-oxazol-4-yl}ethanone (2d)

Yield 94%, brown solid, Mp 64-65 °C. ¹H NMR (300 MHz, CDCl₃): δ 1.57-1.81 (m, 6H, (CH₂)₃), 2.78 (s, 3H, CH₃), 4.23-4.37 (s, 6H, CH₂), 7.09-7.23 (m, 4H, H^{arom}). MS, m/z (%): 362, 364 [M]⁺ (15), 282 [M-HBr]⁺ (40). Anal Calcd for C₁₇H₁₉BrN₂O₂, %: C, 56.21; H, 5.27; N, 7.71. Found, %: C, 56.19; H, 5.35; N, 7.80.

2-Bromo-1-[2-(4-methoxyphenyl)-5-methyl-1,3-oxazol-4-yl]ethanone (2e)

Yield 89%, white solid, Mp 112-113 °C. ¹H NMR (300 MHz, CDCl₃): δ 2.70 (s, 3H, CH₃), 3.87 (s, 3H, OCH₃), 4.59 (s, 2H, CH₂), 6.98 (d, $J = 8.9$ Hz, 2H, H^{arom}), 7.96 (d, $J = 8.9$ Hz, 2H, H^{arom}). MS, m/z (%): 309, 311 [M]⁺ (30), 230 [M-Br]⁺ (100). Anal Calcd for C₁₃H₁₂BrNO₃, %: C, 50.34; H, 3.90; N, 4.52. Found, %: C, 50.28; H, 3.95; N, 4.61.

1.3. Synthesis of diarylethenes

Keto ester **1** was prepared according.^{‡‡} Synthesis of the diarylethene **4a** was described earlier.^{§§}

^{‡‡} A. A. Shimkin, V. Z. Shirinian, A. K. Mailian, D. V. Lonshakov, V. V. Gorokhov and M. M. Krayushkin, *Russ. Chem. Bull., Int. Ed.*, 2011, **60**, 139.

^{§§} V. Z. Shirinian, A. G. Lvov, M. M. Krayushkin, E. D. Lubuzh and B. V. Nabatov, *J. Org. Chem.*, 2014, **79**, 3440.

To a solution of keto ester **1** (2.40 g, 10 mmol) in abs. benzene (30 ml) sodium metal (0.23 g, 10 mmol) was added. The mixture was stirred for 2 h and bromo ketone **2** (10 mmol) was then added portionwise. The mixture was kept overnight, then poured into water (150 ml) and extracted with ethyl acetate (3 × 50 ml). The combined organic phases were washed with water (100 ml), dried with magnesium sulfate and evaporated in vacuum. The diketo ester **3** was used further without additional purification.

A solution of KOH (2.80 g, 50 mmol) in water (37 ml) was added to a mixture of diketo ester **3** and ethanol (37 ml). The reaction mixture was refluxed until completion of the reaction (monitored by TLC), then cooled, poured into water (100 ml) and extracted with ethyl acetate (3 × 50 ml). The combined organic phases were washed with water (100 ml), dried with magnesium sulfate and evaporated in vacuum. The residue was purified by column chromatography by light petroleum / ethyl acetate 3:1 and recrystallized from ethanol.

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

Yield 0.95 g (26%), white powder, Mp 187-188 °C. ¹H NMR (300 MHz, CDCl₃): δ 1.85 (s, 3H, CH₃), 2.07 (s, 3H, CH₃), 2.40 (s, 3H, CH₃), 2.61-2.71 (m, 2H, CH₂), 3.08-3.17 (m, 2H, CH₂), 6.53 (s, 1H, H^{thioph}), 7.15 (dd, *J* = 8.4, 8.4 Hz, 2H, H^{arom}), 8.00 (dd, *J* = 5.1, 8.4 Hz, 2H, H^{arom}). ¹³C NMR (75 MHz, CDCl₃): δ 11.17, 14.36, 15.26, 29.32, 34.51, 115.89, 115.97, 116.19, 123.48, 123.52, 126.85, 128.34, 128.45, 128.98, 133.36, 135.20, 135.62, 136.36, 149.01, 159.57, 161.16, 162.49, 165.82, 207.68. IR (KBr), cm⁻¹: 3059, 2924, 2856, 1694, 1629, 1500, 1225, 1187, 1151. MS, *m/z* (%): 367 (100, [M]⁺), 352 (70, [M-CH₃]⁺). HRMS (ESI): Found, *m/z*: 368.1108. C₂₁H₁₉FNO₂S. Calculated, *m/z*: 368.1115 [M+H]⁺.

2-(2,5-Dimethylthiophen-3-yl)-3-{5-methyl-2-[4-(trifluoromethyl)phenyl]-1,3-oxazol-4-yl}cyclopent-2-en-1-one (4c)

Yield 1.46 g (35%), white powder, Mp 122-124 °C. ¹H NMR (300 MHz, CDCl₃): δ 1.88 (s, 3H, CH₃), 2.07 (s, 3H, CH₃), 2.41 (s, 3H, CH₃), 2.64-2.71 (m, 2H, CH₂), 3.10-3.19 (m, 2H, CH₂), 6.54 (s, 1H, H^{thioph}), 7.73 (d, *J* = 8.2 Hz, 2H, H^{arom}), 8.13 (d, *J* = 8.2 Hz, 2H, H^{arom}). ¹³C NMR (75 MHz, CDCl₃): δ 11.24, 14.36, 15.25, 29.38, 34.50, 125.80, 125.90, 126.49, 126.79, 128.86, 128.90, 130.24, 133.84, 135.26, 135.95, 135.98, 136.48, 149.78, 160.75, 207.57. IR (KBr), cm⁻¹: 2921, 2859, 1700, 1621, 1325, 1164, 1124, 1074. MS, *m/z* (%): 417 (10, [M]⁺), 402 (10, [M-CH₃]⁺), 173 (100). HRMS (ESI): Found, *m/z*: 418.1073. C₂₂H₁₉F₃NO₂S. Calculated, *m/z*: 418.1083 [M+H]⁺.

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

Yield 1.04 g (24%), yellow powder, Mp 82-83 °C. ¹H NMR (300 MHz, CDCl₃): δ 1.59-1.75 (m, 6H, (CH₂)₃), 1.82 (s, 3H, CH₃), 2.06 (s, 3H, CH₃), 2.40 (s, 3H, CH₃), 2.61-2.68 (m, 2H, CH₂), 3.08-3.16 (m, 2H, CH₂), 3.24-3.33 (m, 4H, (CH₂)₂), 6.54 (s, 1H, H^{thioph}), 6.94 (d, *J* = 8.8 Hz, 2H, H^{arom}), 7.86 (d, *J* = 8.8 Hz, 2H, H^{arom}). ¹³C NMR (75 MHz, CDCl₃): δ 11.17, 14.40, 15.29, 24.39, 25.55, 29.43, 34.56, 49.43, 115.05, 116.74, 126.93, 127.53, 129.13, 132.92, 135.13, 136.20, 147.97, 153.14, 161.06, 162.01, 207.96. IR (KBr), cm⁻¹: 2922, 2853, 1698, 1611, 1505, 1440, 1385, 1262, 1239, 1183, 1127, 1023. MS, *m/z* (%): 432 (40, [M]⁺), 188 (100). HRMS (ESI): Found, *m/z*: 433.1875. C₂₆H₂₉N₂O₂S. Calculated, *m/z*: 418.1944 [M+H]⁺.

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

Yield 0.95 g (25%), white powder, Mp 111-112 °C. ¹H NMR (300 MHz, CDCl₃): δ 1.84 (s, 3H, CH₃), 2.08 (s, 3H, CH₃), 2.41 (s, 3H, CH₃), 2.61-2.69 (m, 2H, CH₂), 3.08-3.17 (m, 2H, CH₂), 3.87 (s, 3H, CH₃), 6.54 (s, 1H, H^{thioph}), 6.98 (d, *J* = 8.8 Hz, 2H, H^{arom}), 7.95 (d, *J* = 8.8 Hz, 2H, H^{arom}). ¹³C NMR (75 MHz, CDCl₃): δ 11.11, 14.30, 15.19, 29.30, 34.45, 55.38, 114.22, 119.84, 126.83, 127.86, 128.08, 129.01, 133.02, 135.08, 135.27, 136.17, 148.37, 160.39, 161.43, 207.72. IR (KBr), cm⁻¹: 2966, 2922, 2842, 1696, 1612, 1502, 1439, 1331, 1256, 1168, 1022. MS, *m/z* (%): 379 (50, [M]⁺), 378 (100, [M-H]⁺), 363 (50, [M-CH₄]⁺), 173 (100). HRMS (ESI): Found, *m/z*: 380.1318. C₂₂H₂₂NO₃S. Calculated, *m/z*: 380.1315 [M+H]⁺.

2. UV-vis spectra of compounds 4a-e

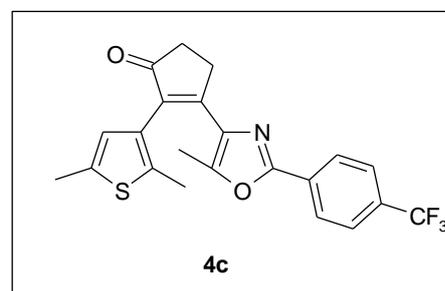
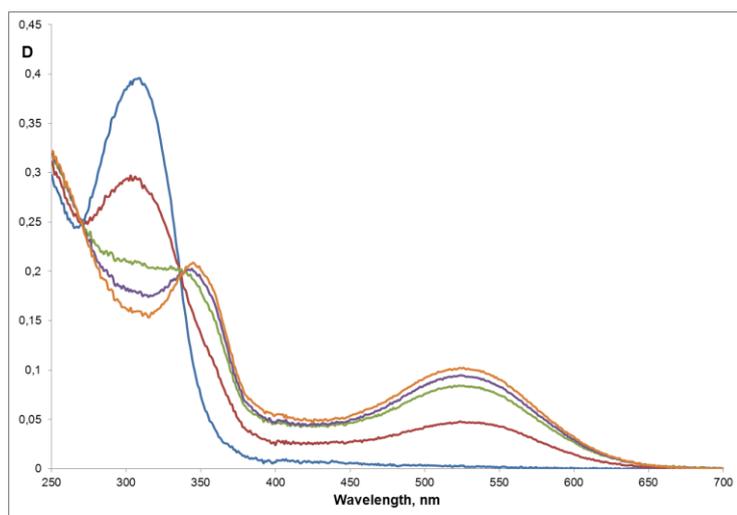
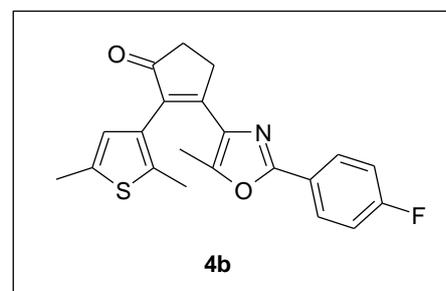
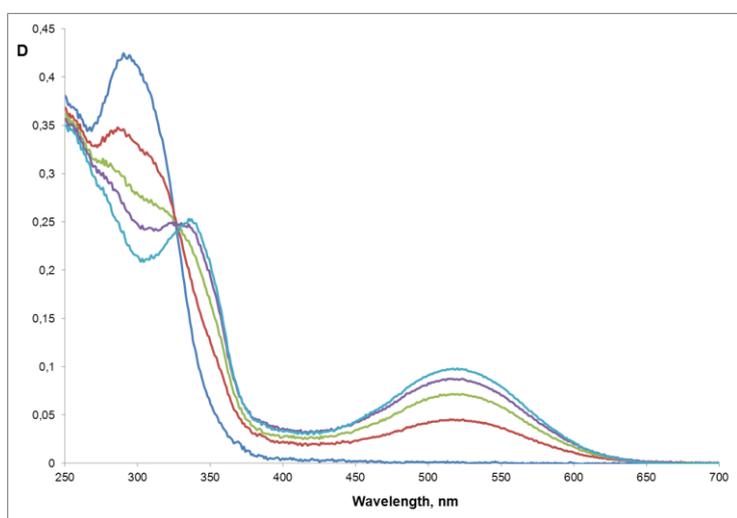
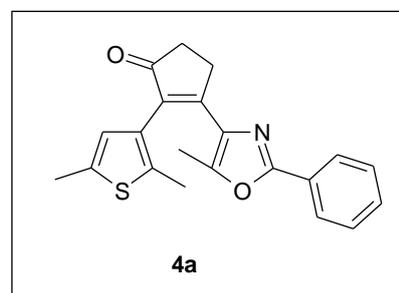
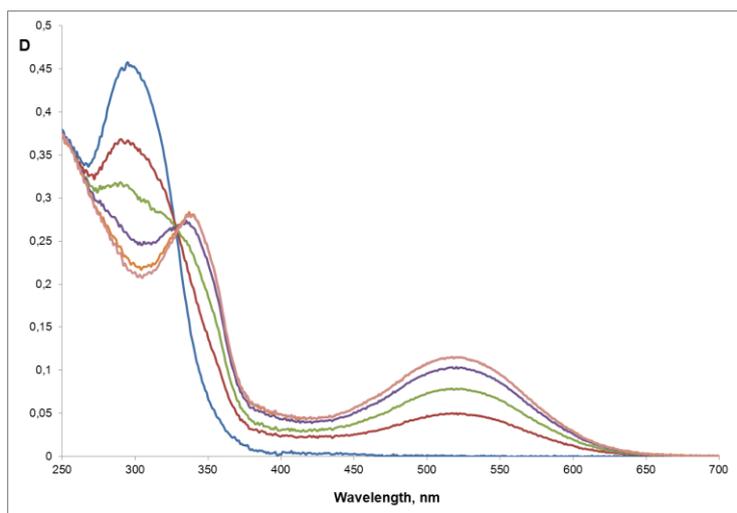


Figure S1. UV-vis absorption spectra during the course of ring-closure of diarylethenes **4a-c** in MeCN ($C \approx 2.5 \times 10^{-5}$ M), induced by irradiation with UV light ($\lambda = 313$ nm) until reaching the photostationary state.

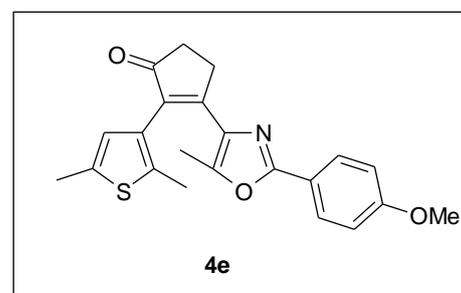
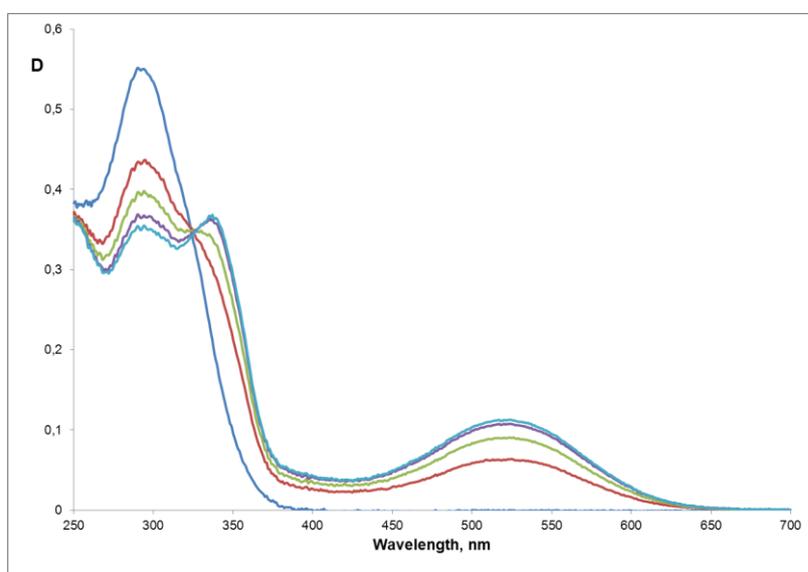
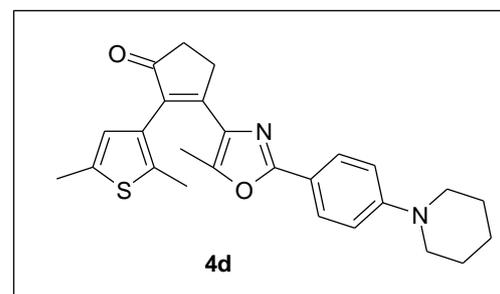
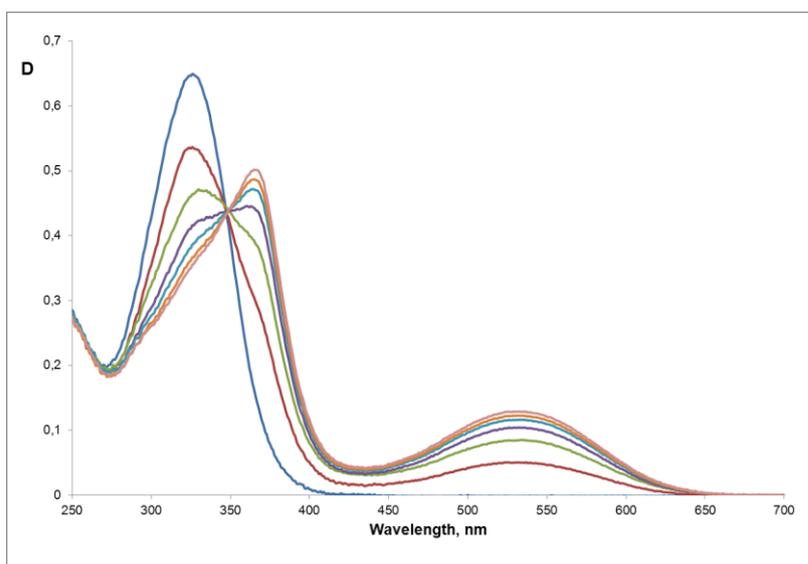


Figure S2. UV-vis absorption spectra during the course of ring-closure of diarylethenes **4d,e** in MeCN ($C \approx 2.5 \times 10^{-5}$ M), induced by irradiation with UV light ($\lambda = 313$ nm) until reaching the photostationary state.

3. NMR signals of initial and photoinduced forms of diarylethenes 4a-e

Table S1. NMR properties of the diarylethenes at 293 K.

№	Open form ^a		Closed form ^b	
	δ (CH ₃)	δ (CH ^{thioph})	δ (CH ₃)	δ (CH ^{thioph})
4a	1.85; 2.07; 2.41	6.54	1.73; 1.76; 2.30	6.84
4b	1.85; 2.07; 2.40	6.54	1.72; 1.75; 2.30	6.84
4c	1.88; 2.07; 2.41	6.54	1.74; 1.76; 2.32	6.86
4d	1.82; 2.06; 2.40	6.54	overlapping, 2.29	6.82
4e	1.84; 2.08; 2.41	6.54	1.71; 1.74; 2.29	6.83

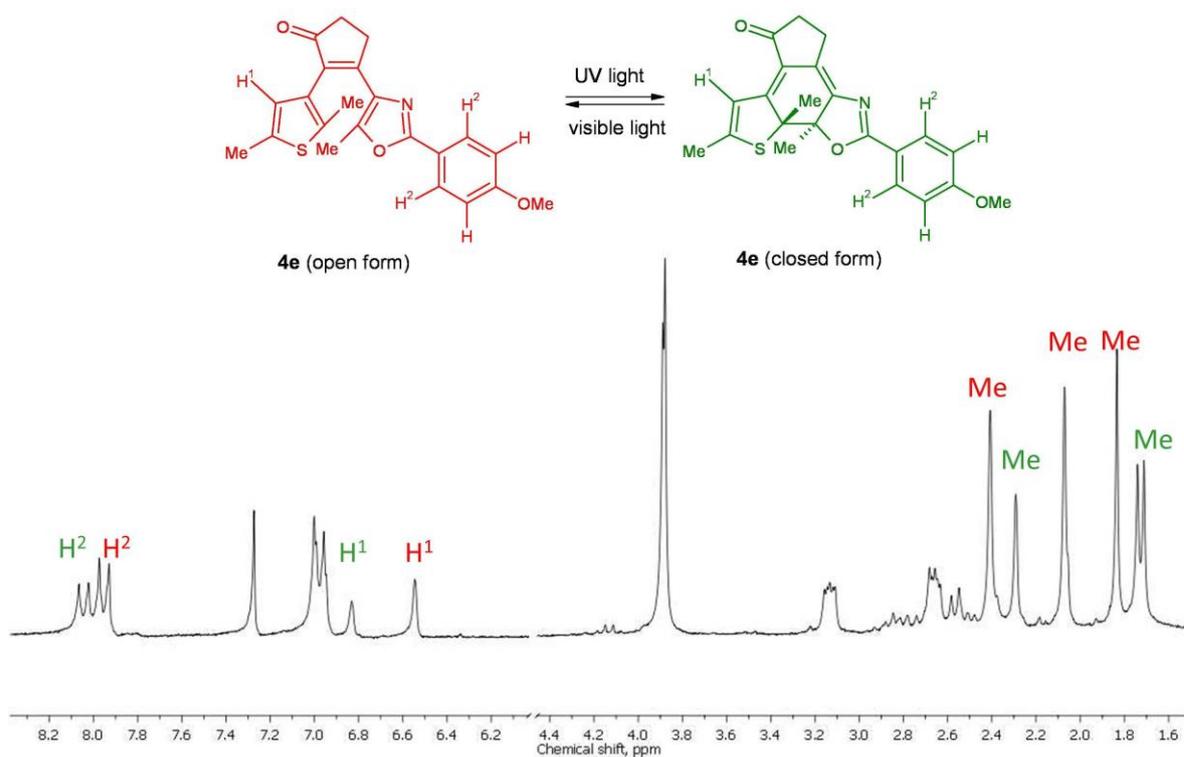


Figure S3. ¹H NMR spectra of compound **4e** after irradiation with 313 nm at r.t. in CDCl₃.

4. Fluorescence modulation for diarylethene 4d

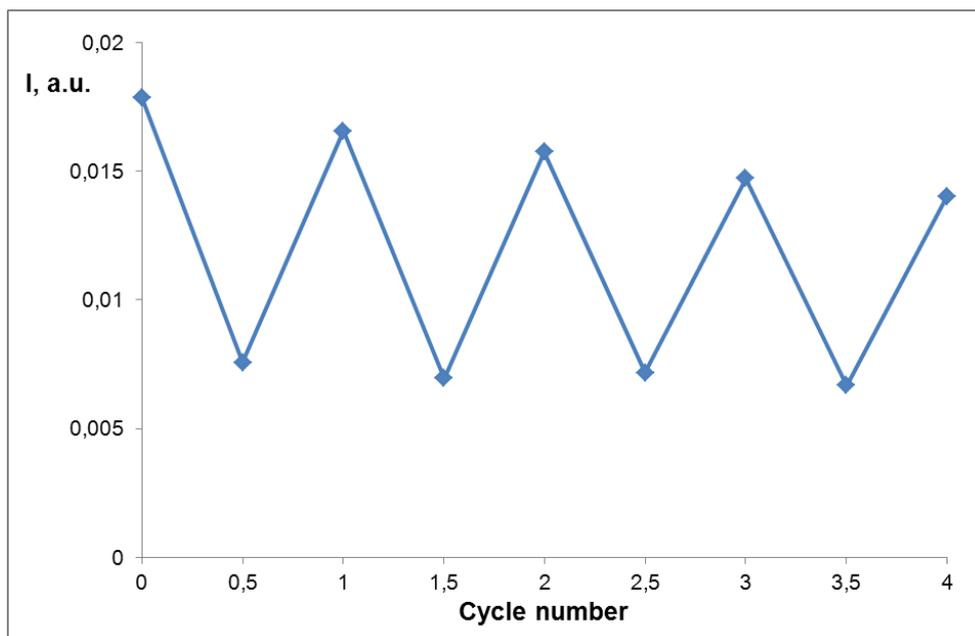
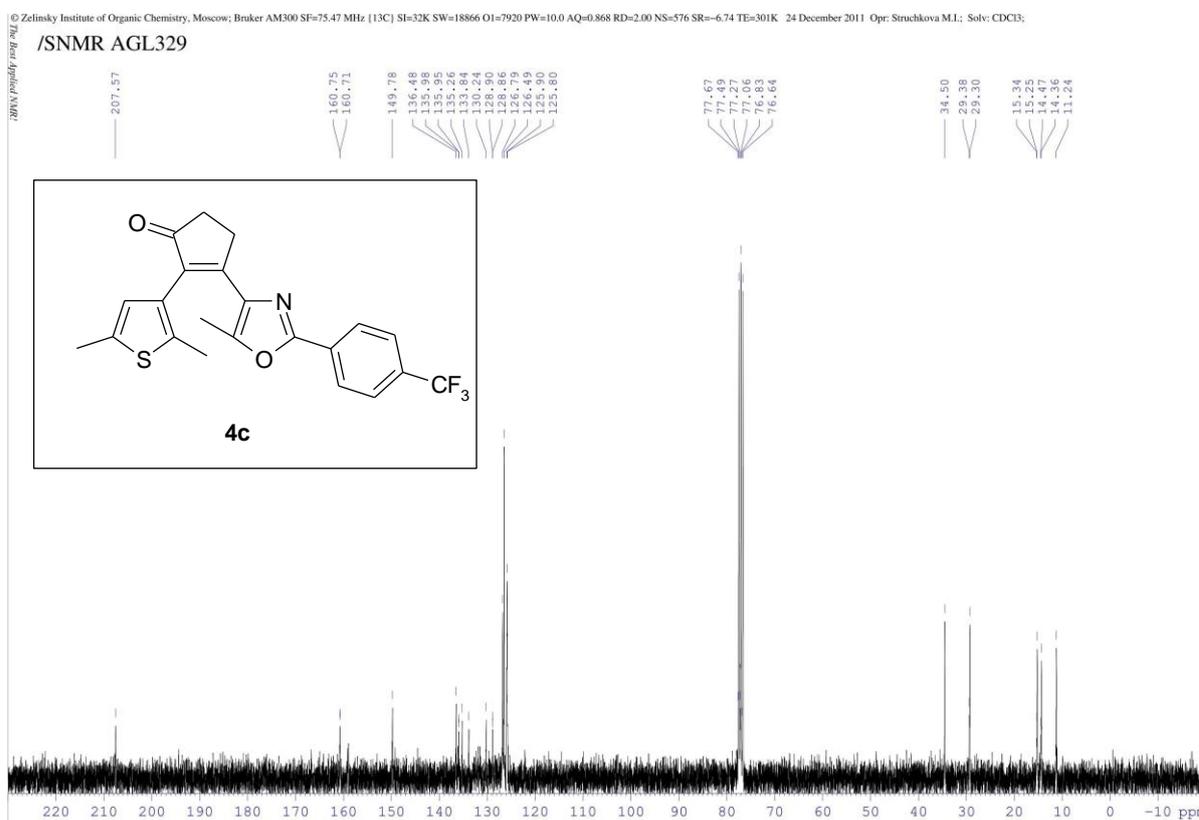
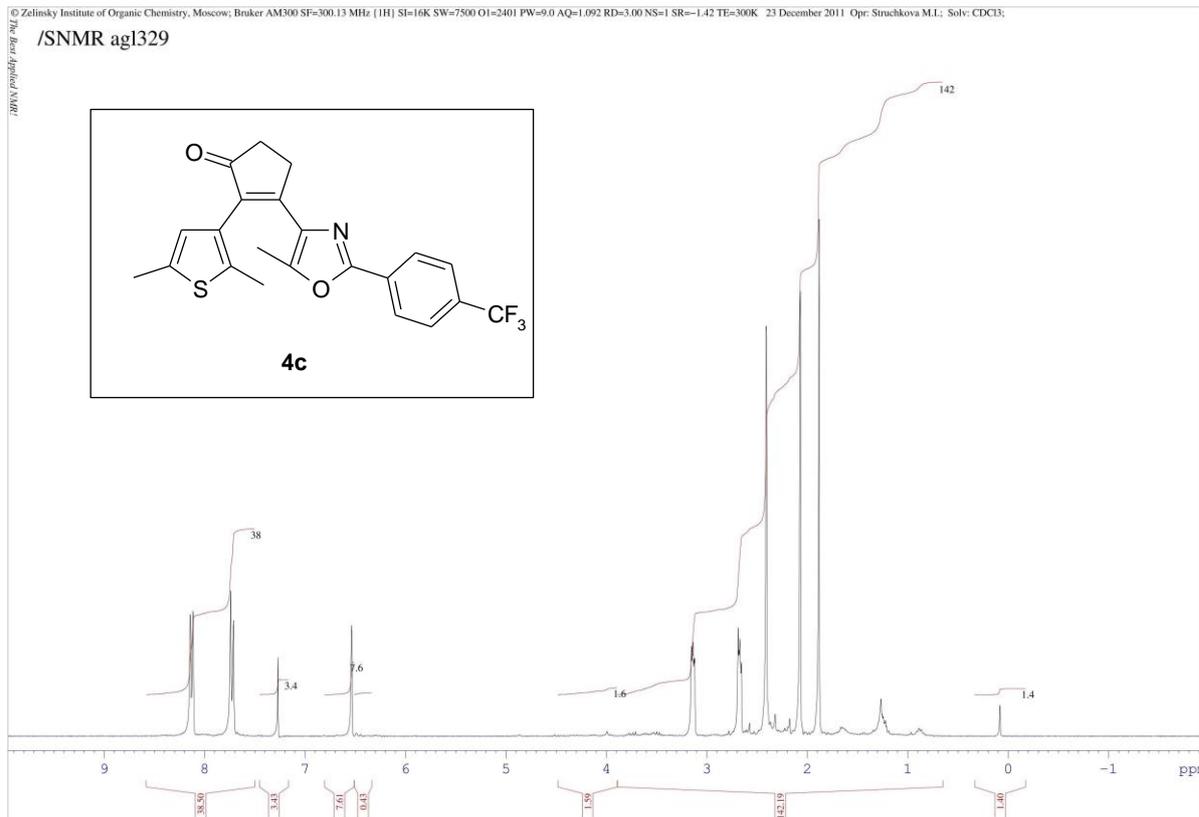
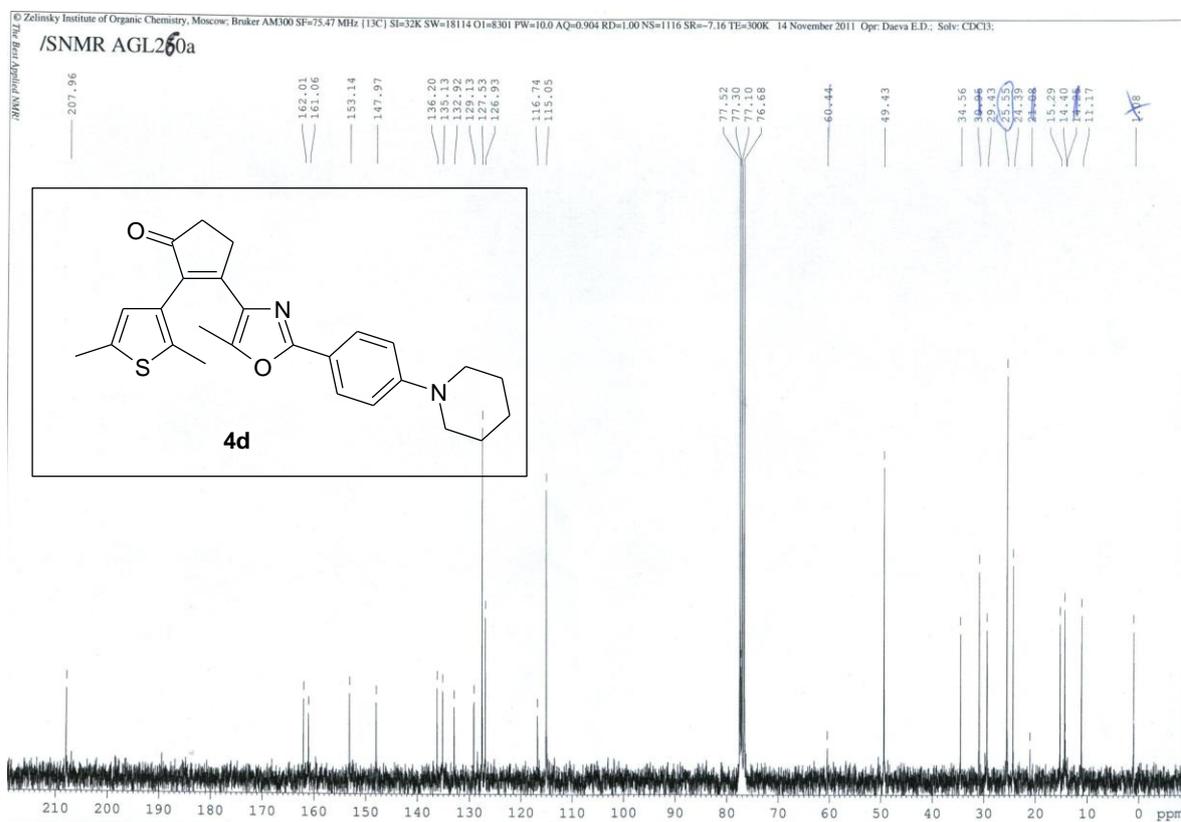
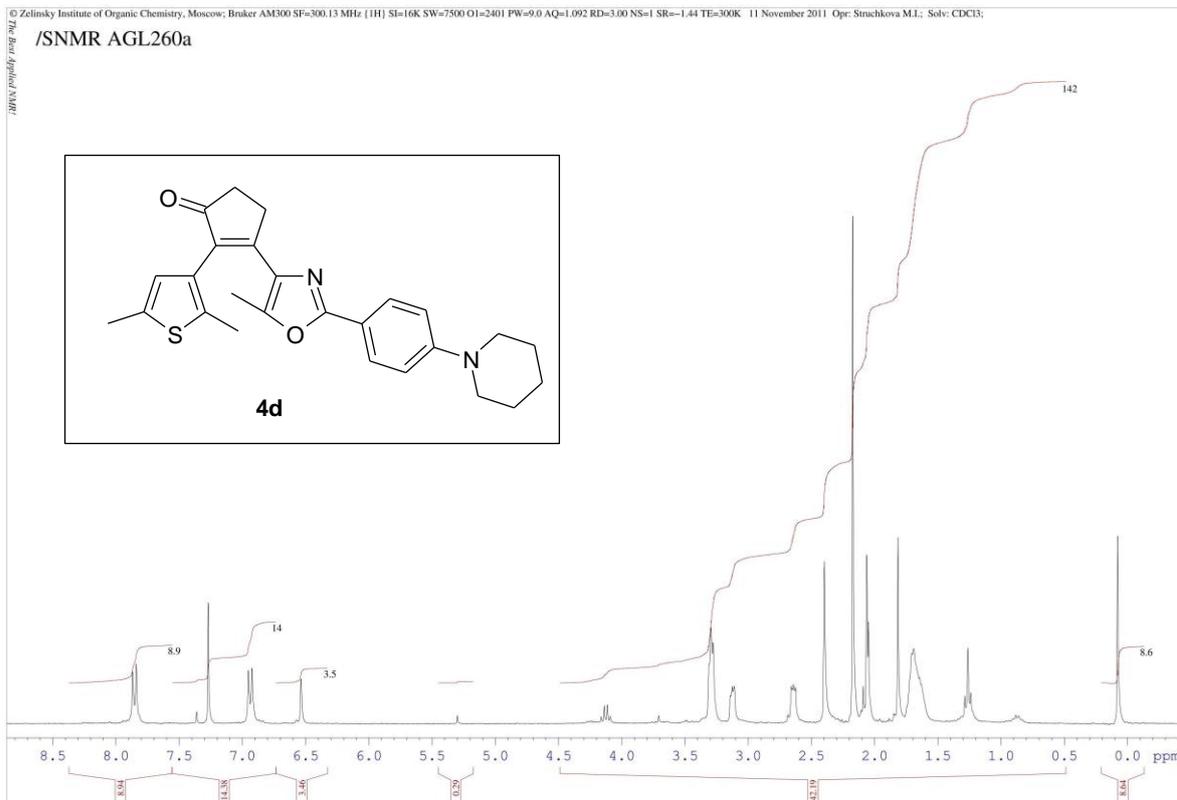


Figure S4. Fluorescence modulation for diarylethene **4d** in MeCN ($C \approx 2.5 \times 10^{-5}$ M) at 293 K under alternative irradiations with 30 s UV irradiation ($\lambda^{\text{ir}} = 313$ nm) and visible light; emission excitation at $\lambda^{\text{ex}} = 326$ nm.

2-(2,5-dimethylthiophen-3-yl)-3-{5-methyl-2-[4-(trifluoromethyl)phenyl]-1,3-oxazol-4-yl}cyclopent-2-en-1-one (4c)



2-(2,5-dimethylthiophen-3-yl)-3-{5-methyl-2-[4-piperidin-1-ylphenyl]-1,3-oxazol-4-yl}cyclopent-2-en-1-one (4d)



2-(2,5-dimethylthiophen-3-yl)-3-[2-(4-methoxyphenyl)-5-methyl-1,3-oxazol-4-yl]cyclopent-2-en-1-one (4e)

