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SHORT COMMUNICATION

Synthesis of methylsulfanyl analogs of Kaede protein chromophore

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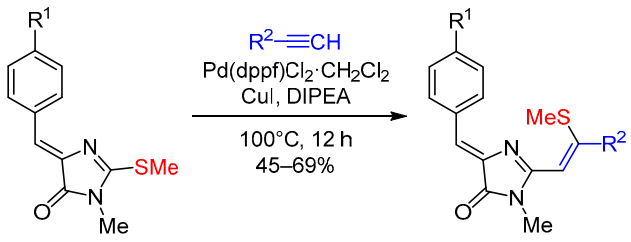


5-Arylidene-1-methyl-2-[2-(methylsulfanyl)-2-phenylethenyl]-1*H*-imidazol-5(4*H*)-ones were synthesized as a result of the reaction of 5-arylidene-1-methyl-2-(methylsulfanyl)-1*H*-imidazol-5(4*H*)-ones with terminal acetylenes in the presence of a palladium catalyst and copper iodide. This reaction presents a rare example of the formation of a compound with a methylsulfanylethenyl group. A study of the optical properties of the obtained compounds showed that they are characterized by a significant bathochromic shift of spectral maxima in comparison with similar derivatives of the GFP chromophore.

Keywords: acetylenes, imidazolones, Kaede protein, chromophores, fluorogens, GFP chromophore.

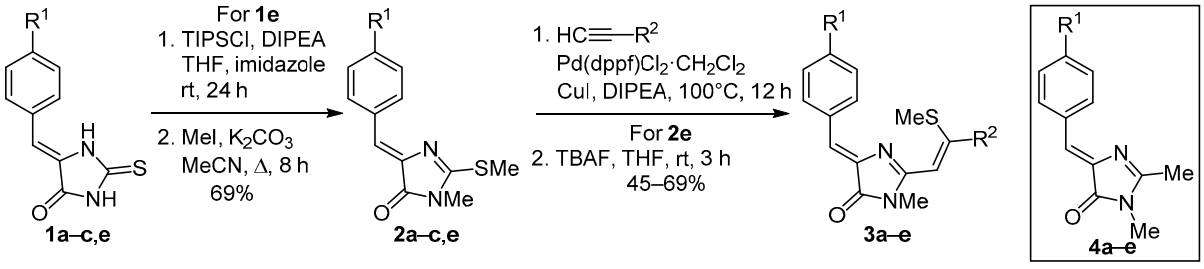
One of the most important modern methods for studying intracellular processes is fluorescence microscopy based on the use of fluorescent dyes. Among them, benzylidene-imidazolones, analogs of the chromophore of green fluorescent protein (GFP), occupy an important place.[1] These compounds are widely used due to the great variability of their optical properties, low toxicity, and synthetic availability.[2,3] One of the subclasses of this group of dyes is the Kaede protein chromophore analogs, which are characterized by a significant bathochromic shift of spectral maxima compared to the original derivatives of the GFP chromophore.[4,5]

It is known that aryl alkyl sulfides can undergo various cross-coupling reactions catalyzed by transition metal complexes.[6] However, very few examples of such reactions with terminal acetylenes are described in the literature. Moreover, these transformations lead to the formation of both substituted acetylenes as a result of the Sonogashira reaction[7,8] and products containing a carbon–sulfur bond.[9,10]

5-Arylidene-2-alkylsulfanylimidazolones **2** are readily available stable reagents.[11] They are structurally similar to the GFP chromophore and were previously used in the synthesis of its derivatives by arylation[12] using metal complex catalysis. The aim of this work was to study the reactions of 5-arylidene-2-methylsulfanylimidazolones **2** with terminal acetylenes.

As a result of our experiments, it turned out that the reaction of 5-arylidene-2-methylsulfanylimidazolones **2**, obtained from 5-arylidene-2-thiooxoimidazolidinones **1**, with acetylenes resulted in the formation of methylsulfanyl compounds **3** (Scheme 1). Moreover, in all cases, no appreciable amounts of acetylene derivative were found in the reaction mixture. Thus, the reaction we have proposed is not only a novel example of the synthesis of the Kaede protein chromophore derivatives, but also a rare example of the creation of a methylsulfanylethenyl group in a molecule. Moreover, we have shown that not only terminal arylacetylenes but also alkylacetylenes can be used in this

Scheme 1



1–4 a R^1 = H, R^2 = Ph; **b** R^1 = NEt_2, R^2 = Ph; **c** R^1 = OMe, R^2 = Ph; **d** R^1 = OMe, R^2 = *n*-Pr
1, **3**, **4 e** R^1 = OH, R^2 = Ph; **2e** R^1 = OTIPS, R^2 = Ph

reaction. We found that the transformation proceeds best in the presence of the Pd(dppf)Cl_2 catalyst, as well as CuI. We used DIPEA as the base, and the reaction was carried out without solvent. In total, we synthesized 5 new compounds.

The structures of the obtained compounds **3**, as well as the configuration of double bonds, were additionally confirmed by the ^{1}H–^{13}C HSQC, ^{1}H–^{13}C HMBC, and ^{1}H–^{15}N HMBC two-dimensional NMR spectroscopy experiments on compound **3c** as an example (Fig. 1). In some cases, the products contained a small inseparable amount of the *E*-isomer (relative to the multiple bond at the sulfur atom) impurity, but its amount rarely exceeded 10%. In the case of compound **3c**, this impurity was also characterized by NMR.

Our studies showed that the revealed transformation does not take place either in the absence of a palladium catalyst or in the absence of CuI. This suggests that the mechanism of this transformation is similar to the classical Sonogashira reaction. However, we did not find the desired arylacetylenes and methanethiol in the reaction products (the reaction was carried out both in a sealed vessel and in a stream of argon, which was supposed to remove this gaseous product). This fact suggests that the methylsulfanyl group does not add to the prepared acetylene according to the nucleophilic mechanism, but is transferred in the catalytic cycle (Scheme 2), as was previously stated.[9]

We studied the optical properties of the new compounds **3a**–**e**, and also performed a comparison with similar derivatives of the GFP chromophore **4a**–**e** (Table 1). The quantum fluorescence yields of all the studied compounds turned out to be small (less than 0.2%), which is typical of such derivatives and facilitates their use as fluorogens.[4,5] A significant bathochromic shift of both the absorption and

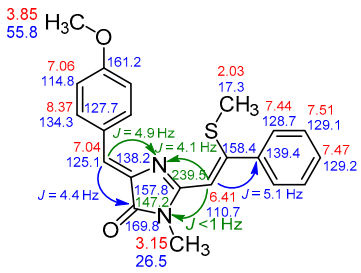
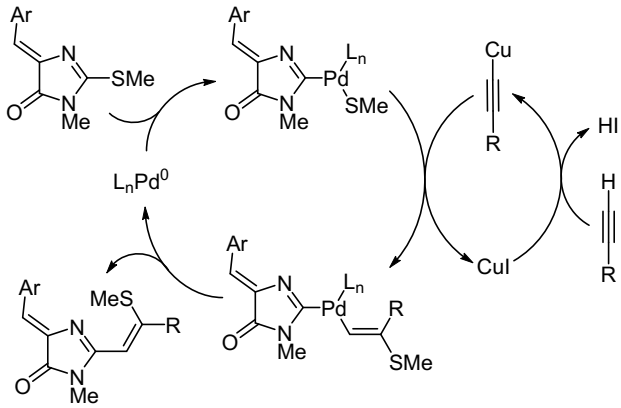


Figure 1. Major correlations and chemical shifts (shifts of ^{1}H are indicated in red, shifts of ^{13}C – in blue, shifts of ^{15}N – in green; δ, ppm) in ^{1}H–^{13}C HSQC, ^{1}H–^{13}C HMBC, and ^{1}H–^{15}N HMBC spectra of compound **3c**.

Scheme 2



emission bands in the spectra of the new compounds **3a**–**e**, compared with compounds **4a**–**e**, as well as an increase in their Stokes shift was noted. The positions of the absorption and emission maxima also depended on the nature of the introduced substituents: the presence of a more donating group in the benzylidene fragment shifted the spectral bands to the long-wavelength region. And in the emission and absorption spectra of compound **3d** (as compared with compound **3c**), a distinct shift of the bands to the shorter wavelength region, as well as a decrease in the Stokes shift could be observed.

To conclude, we have developed a new method for the synthesis of methylsulfanyl analogs of the Kaede protein chromophore as a result of the study. Five new compounds

Table 1. Optical properties of compounds **3a**–**e**, **4a**–**c**,**e** in MeCN

Compound	Absorption maximum, nm	Emission maximum, nm
3a	368	461
3b	486	591
3c	425	541
3d	418	466
3e	425	540
3a	368	461
4a	354	428
4b	425	488
4c	368	435
4e	368	438

were obtained, the optical properties of which suggest the promise of their use as novel dyes. The presence in the composition of all new compounds of the methylsulfanyl group opens up possibilities for even further modification.

Experimental

IR spectra were registered on a Thermo Scientific Nicolet iS10 spectrometer with the Smart iTR attachment. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker Avance III spectrometer (700 and 176 MHz, respectively) in DMSO-d_6, with TMS or the residual solvent signal (2.50 ppm for ^{1}H nuclei and 39.5 ppm for ^{13}C nuclei) as internal standard. High-resolution mass spectra were recorded on a Bruker micrOTOF II, electrospray ionization. Melting points were determined on an SMP 30 apparatus and are uncorrected. All operations with moisture-sensitive substances were carried out in an atmosphere of dry argon using the standard Schlenk technique.

Acros Organics reagents were used without additional purification; freshly distilled solvents were used for the reactions. Compounds **1b**,[13] **1e**,[14] **1**, **2 a**,**c**,[15] **4a**,**b**,[16] **4c**,**e**[17] were synthesized according to literature methods.

(5*Z*)-5-[4-(Diethylamino)benzylidene]-3-methyl-2-(methylsulfanyl)-3,5-dihydro-4*H*-imidazol-4-one (2b). Compound **1b** (825 mg, 3.0 mmol) was dissolved in MeCN (30 ml), MeI (1.70 g, 12.0 mmol) and K_2CO_3 (1.66 g, 12.0 mmol) were added, and the resulting mixture was heated under reflux for 8 h. After cooled, EtOAc (200 ml) was added, and the mixture was washed with saturated aqueous NaCl (3×50 ml). The organic layer was evaporated under reduced pressure, and the product was isolated by column chromatography, eluent $CHCl_3$. Yield 645 mg (71%), red powder, mp 163–165°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.12 (6H, t, *J* = 7.1, 2CH$_2$C$\underline{\text{H}}_3$); 2.69 (3H, s, NCH$_3$); 3.06 (3H, s, SCH$_3$); 3.42 (4H, q, *J* = 7.1, 2C$\underline{\text{H}}_2$CH$_3$); 6.72 (2H, d, *J* = 9.2, H Ar); 6.76 (1H, s, CH=); 8.05 (2H, d, *J* = 8.4, H Ar). ^{13}C NMR spectrum, δ, ppm: 12.4; 12.5; 26.2; 43.8; 111.1; 120.9; 124.3; 133.9; 134.0; 148.7; 160.9; 168.9. Found, *m*/*z*: 304.1474 [M+H]$^+$. $C_{16}H_{22}N_3OS$. Calculated, *m*/*z*: 304.1478.

(*Z*)-3-Methyl-2-(methylsulfanyl)-5-{4-[(triisopropylsilyl)oxy]benzylidene}-3,5-dihydro-4*H*-imidazol-4-one (2e). Compound **1e** (3.0 mmol) was dissolved in THF (50 ml), then triisopropylsilyl chloride (640 mg, 3.3 mmol), DIPEA (490 mg, 3.6 mmol), and imidazole (10 mg) were added. The formed solution was stirred for 24 h and evaporated under reduced pressure. EtOAc (200 ml) was added, and the solution was washed with saturated aqueous NaCl (3×50 ml). The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. Without purification, the residue was dissolved in MeCN (30 ml), MeI (1.70 g, 12.0 mmol) and K_2CO_3 (1.66 g, 12.0 mmol) were added, and the resulting mixture was heated under reflux for 8 h. After cooled, EtOAc (200 ml) was added, and the mixture was washed with saturated aqueous NaCl (3×50 ml). The organic layer was evaporated under reduced pressure, and the product was isolated by column chromatography, eluent $CHCl_3$. Yield 820 mg (69%), yellow powder, mp 160–163°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.07 (18H, d, *J* = 7.3, 3CH(C$\underline{\text{H}}_3$)$_2$); 1.27 (3H, sept, *J* = 7.3, 3C$\underline{\text{H}}$(CH$_3$)$_2$); 2.72 (3H, s, NCH$_3$); 3.08 (3H, s, SCH$_3$); 6.83 (1H, s, CH=); 6.94 (2H, d, *J* = 8.7, H Ar); 8.16 (2H, d, *J* = 8.8, H Ar). ^{13}C NMR spectrum, δ, ppm: 12.1; 12.5; 17.7; 26.3; 120.0; 122.1; 126.5; 133.8; 136.7; 157.1; 161.7; 170.9. Found, *m*/*z*: 405.2022 [M+H]$^+$. $C_{21}H_{33}N_2O_2SSi$. Calculated, *m*/*z*: 405.2027.

Synthesis of compounds 3a–e (General method). Compound **1a–c**,**e** (1 mmol), alkyne (2 mmol), CuI (190 mg, 1 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (41 mg, 0.05 mmol), and DIPEA (2.58 g, 20 mmol) were mixed under an argon atmosphere. The mixture was heated at 100°C in an oil bath for 12 h, cooled, and filtered. EtOAc (200 ml) was added to the filtrate, and the mixture was washed with saturated aqueous NaCl (3×50 ml). The organic layer was evaporated under reduced pressure. In the case of compound **2e**, the intermediate silylated product without additional purification was dissolved in THF (10 ml), $Bu_4NF·3H_2O$ (630 mg, 2 mmol) was added, and the mixture was stirred for 3 h. EtOAc (100 ml) was then added, and the mixture was washed with saturated aqueous NaCl (3×30 ml). The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The product was in all cases isolated by column chromatography, eluent $CHCl_3$ (for compounds **2a**–**d**) or $CHCl_3$–EtOH, 20:1 (for compound **2e**).

(5*Z*)-5-Benzylidene-3-methyl-2-[(*Z*)-2-(methylsulfanyl)-2-phenylethenyl]-3,5-dihydro-4*H*-imidazol-4-one (3a). Content of *E*-isomer less than 5%. Yield 184 mg (55%), yellow powder, mp 158–160°C. IR spectrum, ν, cm^{-1}: 3388, 3065, 2997, 2913, 2432, 2161, 2027, 1978, 1698, 1594, 1495, 1429, 1385, 1314, 1269, 1166, 1032, 961, 753, 688, 584. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.45 (3H, s, SCH$_3$); 2.76 (3H, s, NCH$_3$); 7.02 (1H, s, SC=CH); 7.22 (2H, d, *J* = 7.4, H Ar); 7.25 (1H, s, ArC$\underline{\text{H}}$=); 7.26 (1H, t, *J* = 7.2, H Ar); 7.32 (2H, t, *J* = 7.5, H Ar); 7.42–7.52 (3H, m, H Ar); 8.22 (2H, d, *J* = 6.9, H Ar). ^{13}C NMR spectrum, δ, ppm: 14.9; 26.5; 125.8; 127.4; 128.1; 128.3; 128.6; 128.7; 130.5; 130.6; 132.3; 133.6; 134.9; 138.1; 160.7; 169.3. Found, *m*/*z*: 335.1208 [M+H]$^+$. $C_{20}H_{19}N_2OS$. Calculated, *m*/*z*: 335.1213.

(5*Z*)-5-[4-(Diethylamino)benzylidene]-3-methyl-2-[(*Z*)-2-(methylsulfanyl)-2-phenylethenyl]-3,5-dihydro-4*H*-imidazol-4-one (3b). Content of *E*-isomer less than 3%. Yield 278 mg (69%), red powder, mp 174–176°C. IR spectrum, ν, cm^{-1}: 3066, 2966, 2949, 2433, 2161, 2028, 1977, 1636, 1575, 1428, 1318, 1266, 1189, 1079, 1015, 985, 768, 687, 586. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.14 (6H, t, *J* = 7.0, 2CH$_2$C$\underline{\text{H}}_3$); 2.01 (3H, s, SCH$_3$); 3.14 (3H, s, NCH$_3$); 3.44 (4H, q, *J* = 7.0, 2C$\underline{\text{H}}_2$CH$_3$); 6.39 (1H, s, SC=CH); 6.74 (2H, d, *J* = 9.0, H Ar); 6.95 (1H, s, ArC$\underline{\text{H}}$=); 7.41–7.48 (3H, m, H Ar); 7.48–7.53 (2H, m, H Ar); 8.21 (2H, br. s, H Ar). ^{13}C NMR spectrum, δ, ppm: 12.4; 16.7; 25.9; 43.6; 110.6; 111.2; 121.3; 126.4; 128.2; 128.4; 128.5; 134.2; 134.8; 138.8; 148.8; 154.7; 155.2; 169.0. Found, *m*/*z*: 406.1943 [M+H]$^+$. $C_{24}H_{28}N_3OS$. Calculated, *m*/*z*: 406.1948.

(5*Z*)-5-(4-Methoxybenzylidene)-3-methyl-2-[2-(methylsulfanyl)-2-phenylethenyl]-3,5-dihydro-4*H*-imidazol-4-one (3c). Yield 164 mg (45%), yellow powder, mp 158–160°C.

IR spectrum, ν, cm^{-1}: 3057, 2997, 2932, 2834, 2161, 2028, 1698, 1595, 1506, 1430, 1362, 1110, 1074, 990, 809, 707, 663. Found, *m*/*z*: 365.1318 $[M+H]^+$. $C_{21}H_{21}N_2O_2S$. Calculated, *m*/*z*: 365.1318.

***Z*-Isomer** (34%). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.02 (3H, s, SCH_3); 3.15 (3H, s, NCH_3); 3.84 (3H, s, OCH_3); 6.41 (1H, s, SC=CH); 7.04 (1H, s, ArC<u>H</u>=); 7.05 (2H, d, *J* = 8.8, H Ar); 7.44 (2H, d, *J* = 7.1, H Ar); 7.45–7.52 (3H, m, H Ar); 8.37 (2H, d, *J* = 8.6, H Ar). ^{13}C NMR spectrum, δ, ppm: 17.0; 26.1; 55.4; 110.2; 113.7; 114.4; 124.7; 127.3; 128.3; 128.7; 133.9; 137.6; 138.7; 157.3; 158.1; 160.8; 169.4.

***E*-Isomer** (11%). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.57 (3H, s, SCH_3); 3.19 (3H, s, NCH_3); 3.80 (3H, s, OCH_3); 6.11 (1H, s, SC=CH); 6.74 (1H, s, ArC<u>H</u>=); 6.76 (2H, d, *J* = 8.6, H Ar); 7.35 (2H, d, *J* = 7.2, H Ar); 7.35–7.54 (5H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 15.8; 26.1; 55.2; 105.2; 113.7; 123.8; 127.2; 128.0; 128.1; 128.5; 133.8; 137.5; 138.4; 156.5; 157.1; 160.6; 169.3.

(5*Z*)-5-(4-Methoxybenzylidene)-3-methyl-2-[(*Z*)-3-methyl-2-(methylsulfanyl)but-1-en-1-yl]-3,5-dihydro-4*H*-imidazol-4-one (3d). Content of *E*-isomer 6%. Yield 207 mg (63%), yellow powder, mp 141–143°C. IR spectrum, ν, cm^{-1}: 2917, 2849, 2433, 2160, 2089, 1978, 1698, 1594, 1511, 1446, 1384, 1308, 1253, 1168, 1032, 959, 850, 731, 687, 586. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.01 (3H, t, *J* = 7.3, $CH_2CH_2C\underline{H}_3$); 1.61–1.66 (2H, m, $CH_2C\underline{H}_2CH_3$); 2.48 (3H, s, SCH_3); 2.63–2.67 (2H, m, $C\underline{H}_2CH_2CH_3$); 3.12 (3H, s, NCH_3); 3.83 (3H, s, OCH_3); 6.34 (1H, s, SC=CH); 6.93 (1H, s, ArC<u>H</u>=); 7.02 (2H, d, *J* = 9.0, H Ar); 8.30 (2H, d, *J* = 8.6, H Ar). ^{13}C NMR spectrum, δ, ppm: 13.2; 14.2; 22.6; 25.9; 38.2; 55.2; 114.1; 123.2; 127.3; 133.3; 133.5; 137.7; 157.4; 160.1; 160.4; 169.4. Found, *m*/*z*: 331.1475 $[M+H]^+$. $C_{18}H_{23}N_2O_2S$. Calculated, *m*/*z*: 331.1475.

(5*Z*)-5-(4-Hydroxybenzylidene)-3-methyl-2-[(*Z*)-2-(methylsulfanyl)-2-phenylethenyl]-3,5-dihydro-4*H*-imidazol-4-one (3e). Content of *E*-isomers less than 3%. Yield 168 mg (48%), orange powder, mp 160–162°C. IR spectrum, ν, cm^{-1}: 3152, 2919, 2849, 2601, 2160, 2027, 1674, 1594, 1429, 1362, 1276, 1141, 1028, 934, 762, 695, 596. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.01 (3H, s, SCH_3); 3.14 (3H, s, NCH_3); 6.41 (1H, s, SC=CH); 6.86 (2H, d, *J* = 9.0, H Ar); 6.99 (1H, s, ArC<u>H</u>=); 7.42–7.48 (3H, m, H Ar); 7.51 (2H, d, *J* = 7.4, H Ar); 8.25 (2H, d, *J* = 8.2, H Ar); 10.11 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 16.9; 26.0; 110.3; 115.8; 125.3; 125.8; 128.1; 128.2; 128.6; 134.2; 136.8; 138.7; 155.9; 156.5; 157.4; 159.6; 169.3. Found, *m*/*z*: 351.1154 $[M+H]^+$. $C_{20}H_{19}N_2O_2S$. Calculated, *m*/*z*: 351.1162.

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