SUPPORTING INFORMATION

Synthetic approach to GFP chromophore analogs from 3-azidocinnamates. Role of methyl rotors in the photochemistry.

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I-Experimental Section

A. General

The $^1$H and $^{13}$C NMR spectra were recorded on a 700-MHz Bruker Avance III NMR spectrometer; chemical shifts were referenced to the residual solvent peak. Melting points were taken on a SMP 30 apparatus. UV-VIS spectra were recorded with a Varian Cary 100 spectrophotometer. High resolution mass spectra (HR MS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI).

All chemicals and reagents were purchased from commercial sources. Thin layer chromatography was performed on Merck aluminum sheets. Preparative column chromatography was performed on silicagel 60, 0.060–0.200 mm.
B. Synthesis of methyl 2-azido-3-(4-methoxyphenyl)acrylate (1).

A solution of 4-(methyloxy)benzaldehyde (5.4 g, 40 mmol) and methyl azidoacetate (11.5 g, 100 mmol) in dry methanol (50 mL) was cooled to –30°C. A solution of sodium methoxide in methanol (2.7 M, 30 mL, 80 mmol) was added dropwise (15 min). The reaction mixture was warmed to -5°C and stirred for 5 h, diluted with cold saturated aqueous ammonium chloride (100 mL) and extracted with EtOAc (4 x 100 mL). The combined extracts were washed with water (2 x 100 mL), saturated aqueous sodium chloride (2 x 100 mL) and dried over Na₂SO₄. The solvent was removed in vacuo. The product, a bright yellow solid, was washed with small amount of diethyl ether: (6.1 g, 65%)¹. ¹H NMR (CDCl₃) δ 7.80 (d, J=8.8Hz, 2H), 6.92 (d, J=8.8Hz, 2H), 6.90 (s, 1H), 3.91 (s, 3H), 3.85 (s, 3H).

Synthesis of 2-azido-3-(4-methoxyphenyl)-N-methylacrylamide (3).

A solution of methyl α-azido-4-(methyloxy)cinnamate 1 (11.7 g, 50 mmol) and aqueous methylamine (30 mL, 40%) in ethanol (100 mL) was stirred at room temperature for 48 h. Reaction mixture was evaporated, crude product dissolved in 250 mL of chloroform, washed with aqueous HCl (5%, 100mL), water (2 x 100 mL) and dried over Na₂SO₄. The solution was concentrated in vacuo to give the product, a bright yellow solid, which was washed with hexane and small amount of diethyl ether: (10.7 g, 92%), white solid, mp = 110-115°C with decomposition. ¹H NMR (DMSO-d₆) δ 8.44 (bs, 1H, NH), 7.70 (d, J=8.8Hz, 2H), 6.97 (d, J=8.5Hz, 2H), 6.49 (s, 1H), 3.78 (s, 3H), 2.74 (d, J= 4.3Hz, 3H); ¹³C NMR (DMSO-d₆) δ 26.16 (CH₃), 55.12 (CH₃), 113.90 (2xCH), 118.74 (CH), 126.03, 127.28, 131.18 (2xCH), 159.29, 163.84; HRMS (ESI) m/z: 255.0851 found (calcd. for C₁₁H₁₂N₂NaO₂, [M+H]+ 255.0852).
C. Synthesis of 3-(4-methoxyphenyl)-N-methyl-2-((triphenylphosphanyldene) amino)acrylamide (4).

A solution of amide 3 (2.32 g, 10.0 mmol) and triphenylphosphine (2.9 g, 11.1 mmol) in dry toluene (50 mL) was heated to 65°C under argon. Yellow precipitate formed and effervescence was observed. After 30 minutes reaction mixture was cooled to -10°C. The product, a bright yellow solid, was filtered, washed with small amount of dry toluene and dried in vacuo. (4.10 g, 88%), greenish solid, mp = 203-205°C. 1H NMR (DMSO-d6) δ 8.02 (d, J=8.6Hz, 2H), 7.76 (m, 1H), 7.70 (m, 6H), 7.52 (m, 3H), 7.48 (m, 6H), 6.86 (d, J=8.3Hz, 2H), 5.92 (d, J=7.1Hz, 1H), 3.75 (s, 3H), 2.28 (d, J= 4.3Hz, 3H); 13C NMR (DMSO-d6) δ 25.88 (CH₃), 54.92 (CH₃), 113.14 (2xCH), 128.05 (d, 6CH, J=11.38Hz), 129.22 (2xCH), 130.75 (3xCH), 131.67, 131.89 (d, 6CH, J=9.37Hz), 133.05, 133.63, 140.27, 156.46, 168.91; HRMS (ESI) m/z: 467.1892 found (calcd. for C₂₉H₂₈N₂O₂P, [M+H]^+ 467.1883).
D. General procedure for the preparation of (Z)-4-(4-methoxybenzylidene)-1-methyl-2-alkyl-1H-imidazol-5(4H)-ones (5d, e) from acyl chlorides

A solution of 3-(4-methoxyphenyl)-N-methyl-2-((triphenylphosphanyldene)amino)acrylamide 4 (4.66 g, 10.0 mmol) chloroanhydride (20 mmol) and DIPEA (10 mmol) in dry acetonitrile (50 mL) was stirred for 24 hours at room temperature. After that 200 mL of chloroform was added. The mixture was washed with NaHCO₃ solution (5%, 100 mL), water (2 x 50 mL), saturated aqueous sodium chloride (2 x 50 mL) and dried over Na₂SO₄. The solvent was evaporated and the product was purified by column chromatography (CHCl₃:EtOH=50:1 or EtOAc:hexane=1:1).

(Z)-4-(4-methoxybenzylidene)-1-methyl-2-isopropyl-1H-imidazol-5(4H)-one (5d): 440 mg (17%), yellowish solid, mp = 128-131°C. ¹H NMR (DMSO-d₆) δ 8.21 (d, J=8.76Hz, 2H), 7.02 (d, J=9.0Hz, 2H), 6.96 (s, 1H), 3.82 (s, 3H), 3.13 (s, 3H), 3.00 (m, 1H), 1.27 (d, J=6.6Hz, 6H); ¹³C NMR (CDCl₃) δ 19.62 (2xCH₃), 26.51 (CH), 27.74 (CH₃), 55.33 (CH₃), 114.23 (2xCH), 127.19 (CH), 127.46, 134.24 (2xCH), 137.07, 161.18, 168.25, 171.46; HRMS (ESI) m/z: 259.1439 found (calcd. for C₁₅H₁₉N₂O₂, [M+H]^+ 259.1442).
(Z)-4-(4-methoxybenzylidene)-1-methyl-2-tert-butyl-1H-imidazol-5(4H)-one (5e): 925 mg (34%), yellowish solid, mp = 106-108°C. ¹H NMR (DMSO-d₆) δ 8.22 (d, J=8.8 Hz, 2H), 7.02 (d, J=9.0 Hz, 2H), 7.01 (s, 1H), 3.81 (s, 3H), 3.28 (s, 3H), 1.39 (s, 9H); ¹³C NMR (DMSO-d₆) δ 27.28 (3xCH₃), 28.75 (CH₃), 34.37, 55.26 (CH₃), 114.24 (2xCH), 125.97 (CH), 126.86, 133.98 (2xCH), 136.01, 160.79, 169.67, 170.94; HRMS (ESI) m/z: 273.1602 found (calcd. for C₁₆H₂₁N₂O₂, [M+H]⁺ 273.1598).
E. General procedure for the preparation of (Z)-4-(4-methoxybenzylidene)-1-methyl-2-alkyl-1H-imidazol-5(4H)-ones (5) from carboxylic anhydrides

A solution of amide (3) (2.32 g, 10.0 mmol) and triphenylphosphine (2.9 g, 11.1 mmol) in dry toluene (50 mL) was heated to 65°C under argon. Yellow precipitate formed and effervescence appeared. After 30 minutes reaction mixture was cooled to room temperature and anhydride (20 mmol) and DIPEA (10 mmol) was added. The mixture was heated again and stirred (for conditions see Table S1). The reaction mixture was cooled, and diluted with chloroform (100 mL), washed with NaHCO$_3$ solution (5%, 100mL), water (2 x 50 mL), brine (2 x 50 mL) and dried over Na$_2$SO$_4$. The solvent was evaporated and the product was purified by column chromatography (CHCl$_3$:EtOH=50:1 or EtOAc:hexane=1:1).

Table S1. Conditions for synthesis of (Z)-4-(4-methoxybenzylidene)-1-methyl-2-alkyl-1H-imidazol-5(4H)-ones from carboxylic anhydrides

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<tr>
<td>5a</td>
<td>Me</td>
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<tr>
<td>5b</td>
<td>Et</td>
<td>100°C, 6h</td>
</tr>
<tr>
<td>5c</td>
<td>Pr</td>
<td>100°C, 6h</td>
</tr>
<tr>
<td>5f</td>
<td>CF$_3$</td>
<td>40°C, 1.5h</td>
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</table>

(Z)-4-(4-methoxybenzylidene)-1,2-dimethyl-1H-imidazol-5(4H)-one (5a): 1.40 g (61%)$^2$. $^1$H NMR (DMSO-$d_6$) δ 8.17 (d, J=8.8Hz, 2H), 7.02 (d, J=9.0Hz, 2H), 6.93 (s, 1H), 3.81 (s, 3H), 3.09 (s, 3H), 2.34 (s, 3H).
(Z)-4-(4-methoxybenzylidene)-1-methyl-2-ethyl-1H-imidazol-5(4H)-one (5b): 0.85 g (35%), yellowish solid, mp = 110-113°C. $^{1}$H NMR (DMSO-d$_6$) δ 8.18 (d, J=8.8Hz, 2H), 7.03 (d, J=9.0Hz, 2H), 6.93 (s, 1H), 3.81 (s, 3H), 3.09 (s, 3H), 2.68 (q, J=7.5Hz, 2H), 1.27 (t, J=7.5Hz, 3H); $^{13}$C NMR (DMSO-d$_6$) δ 9.08 (CH$_3$), 21.27 (CH$_2$), 25.88 (CH$_3$), 55.24 (CH$_3$), 114.21 (2xCH), 124.89 (CH), 126.89, 133.77 (2xCH), 136.96, 160.66, 166.33, 169.98; HRMS (ESI) m/z: 245.1278 found (calcd. for C$_{13}$H$_{17}$N$_2$O$_2$, [M+H]$^+$ 245.1285).

(Z)-4-(4-methoxybenzylidene)-1-methyl-2-propyl-1H-imidazol-5(4H)-one (5c): 0.67 g (26%), yellowish solid, mp = 109-112°C. $^{1}$H NMR (DMSO-d$_6$) δ 8.20 (d, J=8.8Hz, 2H), 7.02 (d, J=9.0Hz, 2H), 6.94 (s, 1H), 3.81 (s, 3H), 3.09 (s, 3H), 2.63 (t, J=7.5Hz, 2H), 1.77 (m, J=7.5Hz, 2H), 1.03 (t, J=7.3Hz, 3H); $^{13}$C NMR (CDCl$_3$) δ 13.88 (CH$_3$), 19.05 (CH$_2$), 26.41 (CH$_3$), 30.73 (CH$_2$), 55.31 (CH$_3$), 114.23 (2xCH), 127.15 (CH), 127.36, 134.12 (2xCH), 137.10, 161.18, 164.18, 171.08; HRMS (ESI) m/z: 259.1455 found (calcd. for C$_{15}$H$_{19}$N$_2$O$_2$, [M+H]$^+$ 259.1442).

(Z)-4-(4-methoxybenzylidene)-1-methyl-2-trifluoromethyl-1H-imidazol-5(4H)-one (5f): 1.28 g (45%), yellowish solid, mp = 99-101°C. $^{1}$H NMR (DMSO-d$_6$) δ 8.24 (d, J=9.0Hz, 2H), 7.47 (s, 1H), 7.10 (d, J=8.8Hz, 2H), 3.85 (s, 3H), 3.22 (s, 3H); $^{13}$C NMR (DMSO-d$_6$) δ 26.97 (CH$_3$), 55.50 (CH$_3$), 114.76 (2xCH), 117.61 (sF$_3$, q, J=273.05Hz), 125.69, 133.97 (CH), 134.06, 135.26 (2xCH), 149.10 (q, J=38.15Hz), 162.42, 168.41; HRMS (ESI) m/z: 285.0839 found (calcd. for C$_{13}$H$_{12}$F$_3$N$_2$O$_2$, [M+H]$^+$ 285.0846).
F. Synthesis of (Z)-4-(4-methoxybenzylidene)-1-methyl-1H-imidazol-5(4H)-one (5g).

A solution of amide 3 (5.2 g, 22.4 mmol) and triphenylphosphine (7.0 g, 26.7 mmol) in dry toluene (100 mL) was heated to 65°C under argon. Yellow precipitate formed and effervescence appeared. After 30 minutes reaction mixture was cooled to room temperature and the mixture of formic acid and acetic anhydride (2.9 g of 95% acid and 6.5 g of anhydride, mixed and sustained for 30 min at r.t. before addition) was added. The mixture was heated again to 65°C and stirred for 2 h. After that it was cooled, diluted with 200 mL CHCl₃, washed with NaHCO₃ solution (5%, 100mL), water (2 x 100 mL), brine (2 x 100 mL) and dried over Na₂SO₄. The solvent was evaporated and the product was purified by column chromatography (CHCl₃:EtOH=50:1): (yellowish solid, 1.50 g, 31%), mp = 175-177°C. ¹H NMR (DMSO-d₆) δ 8.20 (d, J=8.6Hz, 2H), 8.13 (s, 1H), 7.02 (d, J=8.8Hz, 2H), 7.08 (s, 1H), 3.82 (s, 3H), 3.12 (s, 3H); ¹³C NMR (DMSO-d₆) δ 27.31 (CH₃), 55.35 (CH₃), 114.36 (2xCH), 126.52, 127.88 (CH), 134.21 (2xCH), 136.77, 155.09 (CH), 161.15, 169.57; HRMS (ESI) m/z: 217.0983 found (calcd. for C₁₂H₁₃N₂O₂, [M+H]⁺ 217.0972).
G. General procedure for phenol demethylation

A solution of (Z)-4-(4-methoxybenzylidene)-1-methyl-2-alkyl-1H-imidazol-5(4H)-one 5 (2.0 mmol) in dry dichloromethane (5 mL) was cooled to 0°C and the solution of boron tribromide in dichloromethane (1M, 3 mL) was added. The mixture was stayed at room temperature for 15 minutes and after that 50 mL of dichloromethane and 20 mL of water was added. The organic layer was washed by saturated aqueous NaHCO₃ (50 mL), water (2 x 50 mL) and dried over Na₂SO₄. The solvent was evaporated and the product was purified by column chromatography (CHCl₃:EtOH = 20:1).

(Z)-4-(4-hydroxybenzylidene)-1,2-dimethyl-1H-imidazol-5(4H)-one (2a): 325 mg (75%) yellow solid. ¹H NMR (DMSO-d₆) δ 10.08 (s, 1H), 8.08 (d, J=8.6Hz, 2H), 6.88 (s, 1H), 6.83 (d, J=8.6Hz, 2H), 3.08 (s, 3H), 2.33 (s, 3H).

(Z)-4-(4-hydroxybenzylidene)-1-methyl-2-ethyl-1H-imidazol-5(4H)-one (2b): 370 mg (80%) yellow solid. ¹H NMR (DMSO-d₆) δ 10.07 (s, 1H), 8.10 (d, J=8.6Hz, 2H), 6.89 (s, 1H), 6.83 (d, J=8.8Hz, 2H), 3.08 (s, 3H), 2.65 (q, J=7.3Hz, 2H), 1.26 (t, 3H, J=7.3Hz).
(Z)-4-(4-hydroxybenzylidene)-1-methyl-2-propyl-1H-imidazol-5(4H)-one (2c): 320 mg (66%), yellow solid, mp = 205-207°C. $^1$H NMR (DMSO-d$_6$) $\delta$ 10.07 (s, 1H), 8.09 (d, J=8.7Hz, 2H), 6.89 (s, 1H), 6.84 (d, J=8.8Hz, 2H), 3.07 (s, 3H), 2.60 (t, J=7.5Hz, 2H), 1.75 (m, 2H), 1.02 (t, J=7.5Hz, 3H); $^{13}$C NMR (DMSO-d$_6$) 13.61 (CH$_3$), 18.26 (CH$_2$), 25.97 (CH$_3$), 29.69 (CH$_2$), 115.66 (2xCH), 125.38, 125.52 (CH), 134.06 (2xCH), 136.18, 159.47, 164.58, 169.95; HRMS (ESI) m/z: 245.1277 found (calcd. for C$_{14}$H$_{17}$N$_2$O$_2$, [M+H]$^+$ 245.1285).

(Z)-4-(4-hydroxybenzylidene)-1-methyl-2-isopropyl-1H-imidazol-5(4H)-one (2d): 375 mg (77%), yellow solid, mp = 176-178°C. $^1$H NMR (DMSO-d$_6$) $\delta$ 10.08 (s, 1H), 8.11 (d, J=8.7Hz, 2H), 6.92 (s, 1H), 6.85 (d, J=8.8Hz, 2H), 3.11 (s, 3H), 2.97 (m, 1H), 1.26 (d, J=6.9Hz, 6H); $^{13}$C NMR (DMSO-d$_6$) 19.38 (2xCH$_3$), 26.08, 26.70 (CH$_3$), 115.68 (2xCH), 125.39, 125.78 (CH), 134.17 (2xCH), 136.02, 159.52, 168.66, 170.28; HRMS (ESI) m/z: 245.1288 found (calcd. for C$_{14}$H$_{17}$N$_2$O$_2$, [M+H]$^+$ 245.1285).

(Z)-4-(4-hydroxybenzylidene)-1-methyl-2-tert-butyl-1H-imidazol-5(4H)-one (2e): 455 mg (88%), yellow solid, mp = 193-196°C. $^1$H NMR (DMSO-d$_6$) $\delta$ 10.16 (s, 1H), 8.11 (d, J=8.6Hz, 2H), 6.96 (s, 1H), 6.84 (d, J=8.8Hz, 2H), 3.28 (s, 3H), 1.39 (s, 9H); $^{13}$C NMR (DMSO-d$_6$) $\delta$ 27.30 (3xCH$_3$), 28.72 (CH$_3$), 34.32, 115.69 (2xCH), 125.34, 126.58 (CH), 134.27 (2xCH), 135.22, 159.64, 168.99, 170.95; HRMS (ESI) m/z: 259.1454 found (calcd. for C$_{15}$H$_{19}$N$_2$O$_2$, [M+H]$^+$ 259.1442).
(Z)-4-(4-hydroxybenzylidene)-1-methyl-2-trifluoromethyl-1H-imidazol-5(4H)-one (2f): 355 mg (66%), yellow solid, mp = 230-250°C with decomposition. $^1$H NMR (DMSO-d$_6$) δ 10.52 (s, 1H), 8.14 (d, J=8.1Hz, 2H), 7.41 (s, 1H), 6.91 (d, J=8.1Hz, 2H), 3.21 (s, 3H); $^{13}$C NMR (DMSO-d$_6$) δ 26.95 (CH$_3$), 116.25 (2хCH), 117.65 (sF$_3$, q, J=273.72Hz), 124.26, 133.13 (CH), 134.67, 135.72 (2хCH), 148.45 (q, J=38.8Hz), 161.62, 168.40; HRMS (ESI) m/z: 271.0686 found (calcd. for C$_{12}$H$_{10}$F$_3$N$_2$O$_2$, [M+H]$^+$ 271.0689).

(Z)-4-(4-hydroxybenzylidene)-1-methyl-1H-imidazol-5(4H)-one (2g): 320 mg (80%), yellow solid, mp = 230-250°C with decomposition. $^1$H NMR (DMSO-d$_6$) δ 10.2 (s, 1H), 8.09 (d, J=8.6Hz, 2H), 8.08 (s, 1H), 7.02 (s, 1H), 6.83 (d, J=8.6Hz, 2H), 3.11 (s, 3H); $^{13}$C NMR (DMSO-d$_6$) δ 27.29 (CH$_3$), 115.82 (2хCH), 125.03, 128.48 (CH), 134.54 (2хCH), 136.02, 154.43 (CH), 160.05, 169.57; HRMS (ESI) m/z: 203.0818 found (calcd. for C$_{11}$H$_{11}$N$_2$O$_2$, [M+H]$^+$ 203.0815).

H. Synthesis of (Z)-4-(4-hydroxybenzylidene)-2-methyl-1H-imidazol-5(4H)-one (2h)

(Z)-2-methyl-4-(4-acetoxybenzylidene)oxazol-5(4H)-one$^5$ (12.3 g, 0.05 mole) was suspended in ethanol (50 mL) and saturated water solution of ammonia (8 mL) was added. The mixture was stirred for 30 min at r.t. Potassium carbonate (6.9 g, 0.05 mole) was added and the mixture was refluxed for 3 hours, diluted with water (300 mL) and acidified to pH 4 by addition of hydrochloric acid (10% aqueous solution). The precipitate was filtered, washed with water (2 x 100 mL), ethanol (30 mL) and diethyl ether (2 x 50 mL); (4.9 g, 50%), yellow solid, mp = 263-
267°C. $^1$H NMR (DMSO-d$_6$) δ 11.14 (s, 1H), 10.01 (s, 1H), 8.04 (d, J=8.6Hz, 2H), 6.82 (d, J=8.8Hz, 2H), 6.75 (s, 1H), 2.21 (s, 3H); $^{13}$C NMR (DMSO-d$_6$) 16.01 (CH$_3$), 115.66 (2xCH), 124.20 (CH), 125.42, 133.80 (2xCH), 137.55, 159.28, 161.48, 171.63; HRMS (ESI) m/z: 203.0858 found (calcd for C$_{11}$H$_{11}$N$_2$O$_2$, [M+H]$^+$ 203.0816).
**II-Spectroscopic and other data**

pKa’s of compounds 2a-h were measured by titration of 2*10^-5 M chromophore solution in 0.2 M phosphate buffer. The calculation was based on absorption half-high (HH) and linear regression (LR) between [H+] and (1-α)/α (where α is the normalized absorption (for anionic form) or absorption (for cationic form)). The results are presented in the tables:

Table S2. pKa of phenolic group

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<th>Compound</th>
<th>pKa(HH)</th>
<th>pKa(LR)</th>
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<td>2e</td>
<td>7.7</td>
<td>7.65</td>
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<td>2f</td>
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Table S3. pKa of imidazolone

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<th>pKa(LR)</th>
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<td>2g</td>
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<td>2h</td>
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<td>2.15</td>
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* - compound is unstable in acidic (pH<2.5) water solution
Fig. S1. Absorbance spectra of \(2a\) at different pH

Fig. S2. Absorbance spectra of \(2e\) at different pH
Fig. S3. Absorbance spectra of 2f at different pH

Fig. S4. Absorbance spectra of 2g at different pH
Fig. S5. Absorbance spectra of 2h at different pH


