DOI: 10.1002/ejoc.201100228

Functionalized Fulgides and Fluorophore-Photoswitch Conjugates

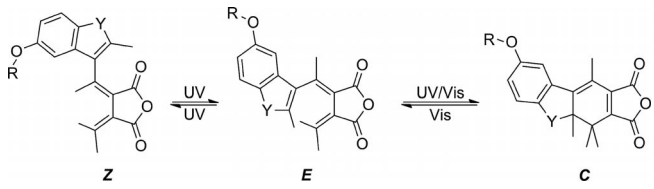
Frank Strübe,[a] Susann Rath,[a] and Jochen Mattay*[a]

Keywords: Fulgides / Photochemistry / Photochromism / Click chemistry / Fluorescence

Various fulgides based on benzofuryl and indolyl core units with versatile functionalities were synthesized. Substitution at the phenylic site shows only small effects on the photochromic properties compared to the parent compounds **30** and **31**. Fulgide–dye conjugates were prepared based on anthryl and coumaryl moieties. Fluorophores were introduced to the fulgide via substitution reaction or copper-catalyzed azide-alkyne cycloaddition (CuAAC). The synthesized conjugates show weak fluorescence and quenching properties in solution.

Introduction

Organic photochromic materials have attracted a lot of attention during the last decades,[1] e.g. for data storage,[2] molecular energy transfer reactions,[3] and high resolution fluorescence microscopy.[4] Due to their inherent switching characteristics (Scheme 1), fulgides have a high potential for manifold applications.[5] These applications require efficient photoswitching and high thermal[6] and photochemical[7] stability of the photochromic compounds. Herein we present the synthesis of fulgides with versatile molecular connecting options based on benzofuryl and indolyl core structures. Different functionalities were introduced by substitution at the phenylic site, e.g. carboxylic acid, alkene or alkyne moieties. These groups offer a wide range of binding options to any target molecule, e.g. to polymers[8,9] and dyes. For fluorescence switching purposes, we synthesized and investigated fulgides linked to fluorophores such as anthracene and coumarin via substitution or copper-catalyzed azide–alkyne cycloaddition (CuAAC). Modulation of the fluorophores' emission intensities should be possible by switching the fulgide moieties between their open and closed forms.



Scheme 1. Photochromism of functionalized heterocyclic fulgides (Y = O or NMe, R = see Table 1).

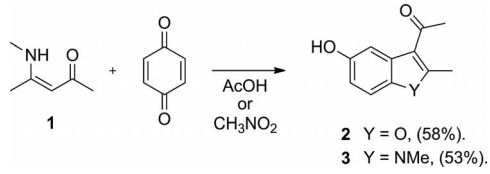
[a] Organische Chemie I, Universität Bielefeld,
Postfach 100131, 33501 Bielefeld, Germany
Fax: +49-521-1066417
E-mail: mattay@uni-bielefeld.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201100228.

Results and Discussion

Synthesis

The benzofuryl and indolyl core units were synthesized in Nenitzescu type reactions (Scheme 2).[10] Using glacial acetic acid as the solvent gave **2** only, whereas a mixture of **3** and **2** was obtained using nitromethane as the solvent. The indolyl compound **3** was purified by recrystallization from methanol.

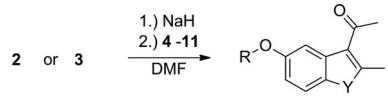


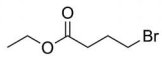
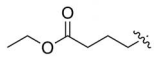
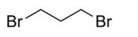
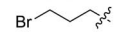
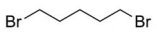
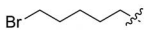
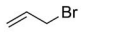
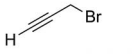
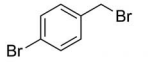
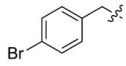
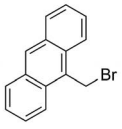
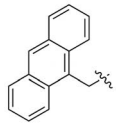
Scheme 2. Nenitzescu-type reaction to form benzofuryl **2** and indolyl **3** precursors.

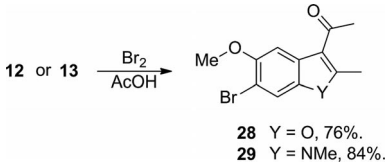
For further functionalization, **2** and **3** were dissolved in dimethylformamide, and the hydroxyl group was deprotonated with sodium hydride, followed by substitution with halides **4**–**11** to give compounds **12**–**27** (Table 1). In general, the substitution products **12**–**27** were obtained in yields of 65–82%. In the reaction with 1,3-dibromopropane (**6**), the monosubstitution products **16** and **17** were formed in small amounts. Instead, dehydrobromination was the main reaction, leading to **20** and **21**. Hence these bromo compounds were left out from further investigation. Bromination of **12** and **13** gave compounds **28** and **29**, respectively (Scheme 3). A second bromination at the acetylic moiety of benzofuryl compound **12** was also observed, which could be suppressed by higher dilution and slow addition of bromine.

The benzofuryl and indolyl precursors were used in Stobbe condensations[11] to obtain the fulgides listed in Table 2. Condensation with diethyl isopropylidenesuccinate[12] was performed in THF at –78 °C using lithium diisopropylamide (LDA) as the base. Intermediate products

Table 1. List of substituted ketones.



Substrate	Product	
Me—I **4**	Me-	**12** Y = O, 82%. **13** Y = NMe, 79%.
 **5**		**14** Y = O, 67%. **15** Y = NMe, 65%.
 **6**		**16** Y = O **17** Y = NMe
 **7**		**18** Y = O, 81%. **19** Y = NMe, 77%.
 **8**		**20** Y = O, 82%. **21** Y = NMe, 80%.
 **9**		**22** Y = O, 79%. **23** Y = NMe, 76%.
 **10**		**24** Y = O, 71%. **25** Y = NMe, 66%.
 **11**		**26** Y = O, 82%. **27** Y = NMe, 70%.



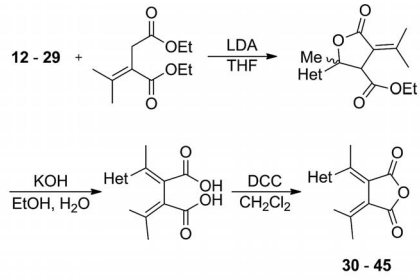
28 Y = O, 76%.
29 Y = NMe, 84%.

Scheme 3. Bromination of **12** and **13**.

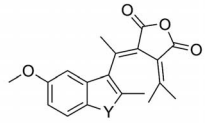
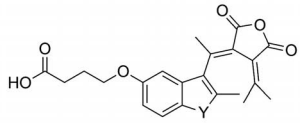
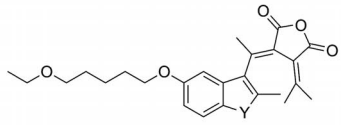
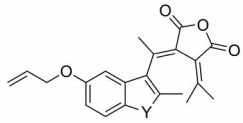
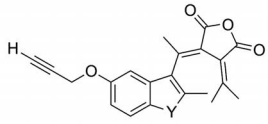
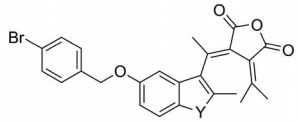
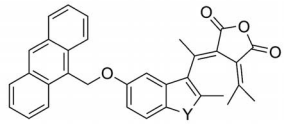
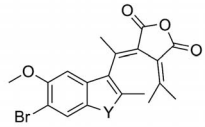
were only detected by TLC and were subsequently treated with potassium hydroxide for saponification and dicyclohexylcarbodiimide for anhydride formation. Fulgides were purified by column chromatography with mixtures of cyclohexane and ethyl acetate and recrystallization from suitable solvents. The photochromic compounds were obtained in yields of 5–15%.[13]

Saponification of the ester functionality of **14** and **15** occurred as a side reaction, leading to carboxylic acids **32** and **33**. During the saponification step, the bromo compounds **18** and **19** underwent substitution reactions with ethoxide, yielding the corresponding ether derivatives **34** and **35**. Furthermore, the synthesis of the alkyne fulgide **38** was not successful. Formation of a photochromic compound was observed by TLC, but it could not be isolated and characterized.

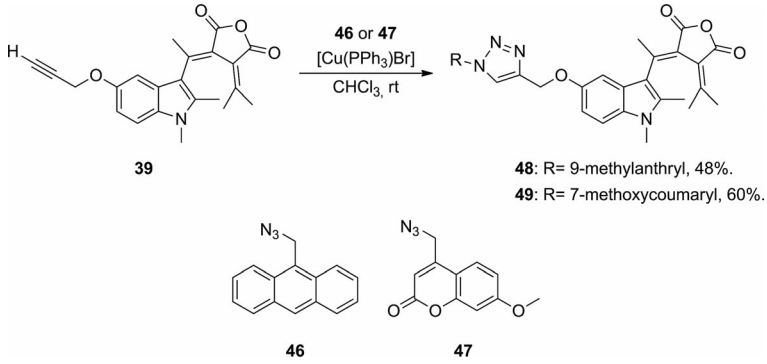
Table 2. Stobbe condensation[11] of ketones **12**–**29** and diethyl isopropylidenesuccinate[12] and subsequent saponification and dehydration to form fulgides **30**–**45**. Ketones **16** and **17** were left out from the investigation.



30 - 45

Substrate	Product	
12 Y = O **13** Y = NMe		**30** Y = O, 7%. **31** Y = NMe, 9%.
14 Y = O **15** Y = NMe		**32** Y = O, 6%. **33** Y = NMe, 7%.
18 Y = O **19** Y = NMe		**34** Y = O, 5%. **35** Y = NMe, 8%.
20 Y = O **21** Y = NMe		**36** Y = O, 11%. **37** Y = NMe, 8%.
22 Y = O **23** Y = NMe		**38** Y = O **39** Y = NMe, 7%.
24 Y = O **25** Y = NMe		**40** Y = O, 13%. **41** Y = NMe, 15%.
26 Y = O **27** Y = NMe		**42** Y = O, 10%. **43** Y = NMe, 8%.
28 Y = O **29** Y = NMe		**44** Y = O, 7%. **45** Y = NMe, 9%.

The new fulgides offer versatile connecting options to biomolecules, polymers and fluorophores. For example, by activation of the carboxylic acid function, **32** and **33** may



Scheme 4. Copper-catalyzed azide–alkyne cycloaddition.

be linked to amines. Cross coupling reactions[14] make way for further functionalization of the bromo compounds **40/41** and **44/45**. To demonstrate, we subjected the alkyne fulgide **39** to "click" reactions with azide dyes.[15] Anthracene and coumarin azides were used as fluorophores, and were prepared according to the literature.[16] 9-(Azidomethyl)-anthracene (**46**) was prepared from 9-(hydroxymethyl)-anthracene by bromination and subsequent treatment with sodium azide.[17] 4-Azidomethyl-7-methoxycoumarin (**47**) was synthesized in a Pechmann reaction starting from 3-methoxyphenol and 4-chloroacetoacetate and further treatment with sodium azide.[18] The triazole formation between the azides and alkyne **39** was catalyzed by $[Cu(PPh_3)_3Br]$[19] in chloroform solution at room temperature (Scheme 4). The cycloaddition products were obtained in moderate yields of 48% and 60%.

Photochemistry

In this study, only the (*E*)-forms of the fulgides were isolated and investigated. The photochemical properties of the synthesized fulgides were analyzed by UV/Vis spectroscopic methods in dichloromethane solutions. In addition, fluorophore–fulgide conjugates were investigated by emission spectroscopy. Complete absorption and emission spectra of **42/43** and **48/49** are available in the Supporting Information. All fulgides showed reversible photoswitching behavior (*e.g.* **39**, see Figure 1). As expected, substitution at the 5-position of the heterocyclic moiety showed only small effects on the absorption of the fulgides (Table 3).

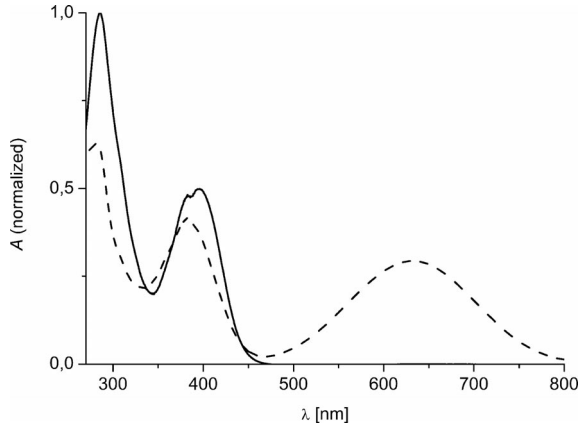


Figure 1. Absorption spectrum of **39**. Solid line: 10^{-4} M solution in dichloromethane; dashed line: after 5 min irradiation with $\lambda_{E\rightarrow C}$ = 405 nm light.

Table 3. UV/Vis data of the synthesized fulgides.

Compound	λ_{max} [nm] (ε [L mol^{-1} cm^{-1}]) of ***E***	λ_{max} [nm][a] of ***C***
30	339 (7200)	506
31	396 (10500)	645
32	337 (5900)	508
33	397 (5500)	643
34	332 (8000)	504
35	399 (9300)	646
36	338 (7200)	507
37	397 (8600)	642
39	396 (8600)	635
40	339 (7400)	505
41	396 (9300)	639
42	387 (8600), 367 (12000), 348 (11400), 334 (9300)[b]	506
43	393 (9300),[b] 387 (13700), 368 (13000), 350 (8300), 330 (6100)	604
44	335 (5300)	511
45	394 (9700)	628
48	389 (13100), 369 (13600), 350 (8800), 334 (6100)[b]	639
49	395 (8700)	638

[a] After 5 min irradiation with $\lambda_{E\rightarrow C}$ = 365 or 405 nm light, respectively. [b] Superimposed by the anthracene absorption bands.

Typically the benzofuryl compounds showed absorption maxima at 332–339 nm for the open (*E*)-form, and at 504–511 nm for the closed (*C*)-form in the photostationary state upon irradiation with $\lambda_{E\rightarrow C}$ = 365 nm light. For the indolyl fulgides, the absorption maxima were bathochromically shifted to 393–399 nm for the (*E*)-form and to 604–646 nm for the closed (*C*)-form in the photostationary state upon irradiation with $\lambda_{E\rightarrow C}$ = 405 nm light. The decoloration could be initiated by irradiation with 530 nm light and 590 or 620 nm light. For the anthracene-containing conjugates, the absorption maxima of the open forms were superimposed by the typical absorption bands of the anthracene moieties.

Modulation of the fluorophores was expected for the fluorophore–fulgide conjugates by switching the photochromic unit between the open and closed form upon irradiation. The anthryl–benzofuryl compound **42** showed the typical anthracene emission pattern between 380–480 nm upon excitation with λ_{ex} = 360 nm light (Figure 2). Irradiation with $\lambda_{E\rightarrow C}$ = 365 nm light decreased the emission to 66%. Reopening of the fulgide with $\lambda_{C\rightarrow E}$ = 530 nm light almost recovered the emission to the starting value. After two switching cycles, the fluorescence increased well beyond the starting value, which indicated decomposition processes.

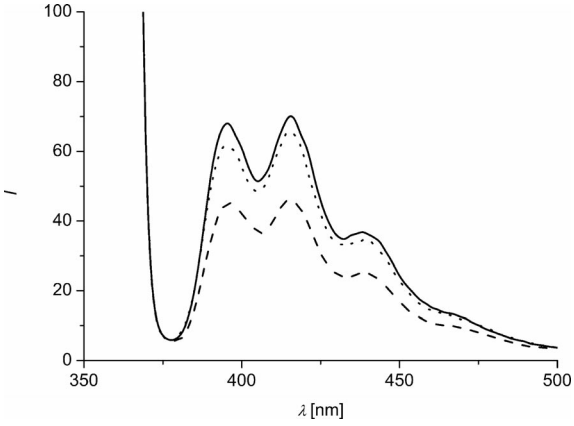


Figure 2. Emission spectrum of **42** (λ_{ex} = 360 nm). Solid line: 3×10^{-6} M in dichloromethane; dashed line: after 20 s irradiation with $\lambda_{E\rightarrow C}$ = 365 nm light; dotted line: after 30 s irradiation with $\lambda_{C\rightarrow E}$ = 530 nm light.

Conjugate **43** showed an inverse emission characteristic compared to **42**. Upon excitation with λ_{ex} = 360 nm light, only very weak fluorescence could be observed between 380–480 nm. Irradiation with $\lambda_{E\rightarrow C}$ = 405 nm light led to an increased emission with a maximum at 415 nm. However, the emission could not be reduced by irradiation with $\lambda_{C\rightarrow E}$ = 620 nm light.

Remarkably, the triazole conjugate **48** showed almost no fluorescence upon excitation with λ_{ex} = 360 nm light, but with excitation at λ_{ex} = 263 nm light, a similar behavior was observed as for **42**. Closing **48** by irradiation at $\lambda_{E\rightarrow C}$ = 405 nm led to a reduced emission at 417 nm to 81%, which could be recovered to the initial value by irradiation with $\lambda_{C\rightarrow E}$ = 620 nm light. Longer irradiation led to decomposition of the conjugate. For the coumaryl compound **49**, little modulation of the fluorescence was achieved. Excitation with λ_{ex} = 335 nm light resulted in fluorescence between 350 and 550 nm. By closing the photochromic unit with $\lambda_{E\rightarrow C}$ = 405 nm light, the emission decreased to 84%. The emission between 350 and 420 nm could be recovered to the initial value upon reopening with $\lambda_{C\rightarrow E}$ = 620 nm light, while the emission between 420 and 550 nm was still reduced.

In a previous study, we investigated fluorescence modulation based on dithienylethene photoswitches.[16] These conjugates also contained coumaryl and anthryl units as fluorophores. The modulation of the emission was very effective, and it could be reduced to 35–10% by switching the dithienylethene into the closed form. Reopening of the photoswitch almost recovered the initial value of the emission. We proposed a resonance energy transfer (RET) or a photoinduced energy transfer mechanisms to be responsible for the quenching processes.

A resonance energy transfer (RET) can be assumed if sufficient spectral overlap between the emission spectra of the fluorophores and the absorption maxima of the photoswitches can be found.[20] For modulation of the emission, a change in the overlap integral must be achieved, for example, by changing the absorption maxima upon closing and reopening the photochromic unit. One drawback of the synthesized fulgides is the undesired photoisomerization between the open (*E*)- and (*Z*)-forms upon irradiation, which could be proved for compound **30**.[21] This competitive reaction to the ***E*→*C*** ring closing reaction could be a reason for the weak modulation of the emission. Additionally, the absorption spectra of the (*C*)-forms still exhibit an intense absorption in the region of the absorption maxima of the (*E*)-forms. Due to low quantum yields for the coloration reaction of indolyl fulgides, the concentration of the (*C*)-form in the photostationary state appears to be small compared to the (*E*)- and (*Z*)-forms.[22] Therefore, there are no remarkable changes in the UV/Vis spectra for the absorption maxima near 400 nm. Due to this, the overlap integrals of the synthesized conjugates exhibit only small differences in the open and closed forms. We assume these absorption characteristics of the photoswitches to be responsible for their low modulation properties.

In further studies the exact mechanisms of the quenching processes should be elucidated. Preliminary NMR experiments indicate that steric factors may play a role for the modulation properties.

Conclusions

We succeeded in synthesizing a variety of novel functionalized benzofuryl and indolyl fulgides. All show photochromic behavior upon alternating irradiation with UV and visible light. We attached fluorophores to an alkyne fulgide via a "click" reaction. The new fluorophore–fulgide conjugates exhibit relatively small effects on the switching behavior of emission. Only for anthryl–benzofuryl fulgide **42** and anthryl–indolyl fulgide **48** a substantial modulation of the emission was achieved.

Experimental Section

General: Commercially available compounds were purchased from Acros, Alfa Aesar, Sigma Aldrich or VWR, and were used as received. Solvents were of analytical grade and dried according to standard procedures. Column chromatography was performed with silica gel (0.040–0.063 mm, Macherey–Nagel). NMR spectra were measured with Bruker DRX 500 and Avance 500 spectrometers, and measured at room temperature. Substances were dissolved in $CDCl_3$ (δ =7.24 ppm/77.0 ppm) or [D_6]DMSO (δ =2.49 ppm/39.5 ppm) and referenced to solvent peaks. EI mass spectra were recorded using an Autospec X magnetic sector mass spectrometer with EBE geometry equipped with a standard EI source. ESI mass spectra were recorded using a Bruker Esquire 3000 ion trap mass spectrometer equipped with a standard ESI/APCI source. HRMS spectra were performed using a Bruker APEX III Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer. Absorption spectra were recorded with a Perkin–Elmer Lambda 40 spectrometer, and fluorescence spectra were recorded with a Perkin–Elmer LS50B spectrometer. For irradiation experiments, LEDs (365, 405, 530, 590 and 620 nm light) were used. The synthesis of the azide precursors **46** and **47** was published before.[16]

(*Z*)-4-Methylaminopent-3-en-2-one (1): Methylamine (10 mL, 0.12 mol, 40% aq. sol.) was added to acetyl acetone (10.30 mL, 0.10 mol), and the mixture was stirred for 2 h at room temperature. After the exothermic reaction ended, the layers were separated, and the aqueous layer was extracted with diethyl ether (2 × 30 mL). The combined organic layers were washed with water and brine and dried with $MgSO_4$. All volatile compounds were removed in vacuo, and the product was recrystallized from diethyl ether. Compound **1** was obtained as colorless needles, which sublimed under high vacuum. Yield: 10.52 g, 90 mmol, 90%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.67 (br. s, 1 H, NH), 4.95 (s, 1 H, CH), 2.89 (d, $^3J_{H,H}$ = 5.1 Hz, 3 H, NCH_3), 1.96 (s, 3 H, CH_3), 1.88 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 194.6, 164.0, 95.0, 29.3, 28.6, 18.5 ppm. MS (EI, 70 eV): *m*/*z* (%) = 113 (50) [M^+], 98 (100) [$M - CH_3^+$], 56 (65), 43 (16), 40 (14).

1-(5-Hydroxy-2-methylbenzofuran-3-yl)-ethanone (2): To a solution of *p*-benzoquinone (2.13 g, 20 mmol) in glacial acetic acid (80 mL), compound **1** (2.33 g, 21 mmol) dissolved in glacial acetic acid (30 mL) was added. In an exothermic reaction, a colorless precipitate was formed after a few minutes. After stirring for 2 h, the precipitate was filtered off, washed with water and dried in vacuo. The product **2** was used without further purification, but could be recrystallized from glacial acetic acid. Yield: 2.19 g, 12 mmol, 58%. ^{1}H NMR (500 MHz, [D_6]DMSO): δ = 9.31 (s, 1 H, OH), 7.35 (m, 2 H, ArH), 6.73 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 2.5 Hz, 1 H, ArH), 2.72 (s, 3 H, CH_3), 2.53 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, [D_6]-DMSO): δ = 193.8, 163.2, 154.3, 146.9, 126.7, 117.1, 112.9, 111.1, 106.4, 30.8, 15.4 ppm. MS (EI, 70 eV): *m*/*z* (%) = 190 (51) [M^+], 176 (11), 175 (100), 147 (13), 43 (20).

1-(5-Hydroxy-1,2-dimethyl-1*H*-indol-3-yl)ethanone (3): To a solution of *p*-benzoquinone (19.11 g, 0.18 mol) in nitromethane (89 mL), compound **1** (20.00 g, 0.18 mol) dissolved in nitromethane (177 mL) was added. A colorless precipitate was formed after stirring for 20 h. The precipitate was filtered off, washed with nitromethane and a small amount of diethyl ether and dried in vacuo. The residue contained a mixture of the indolyl and benzofuryl compounds, and the product **3** was isolated by recrystallization from methanol. Yield: 18.77 g, 94 mmol, 53%. ^{1}H NMR (500 MHz, [D_6]DMSO): δ = 8.97 (s, 1 H, COOH), 7.38 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H, ArH), 7.28 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, ArH), 6.67 (dd, $^3J_{H,H}$ = 8.7, $^4J_{H,H}$ = 2.0 Hz, 1 H, ArH), 3.63 (s, 3 H, CH_3), 2.64 (s, 3 H, CH_3), 2.47 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, [D_6]-DMSO): δ = 192.6, 153.0, 144.8, 130.7, 127.0, 112.9, 111.1, 110.5, 105.4, 31.2, 29.6, 12.6 ppm. MS (EI, 70 eV): *m*/*z* (%) = 203 (36) [M^+], 189 (13), 188 (100). HRMS (EI): calcd. for $C_{12}H_{13}NO_2$ [M^+] 203.09463; found 203.09600.

General Functionalization of 2 and 3: To a stirred solution of **2** or **3** (6 mmol) in dimethyl formamide (DMF, 40 mL), sodium hydride (0.30 g, 7 mmol, 60% susp.) was added at 0 °C under argon. After stirring for 1 h, the appropriate halide **4**–**11** (7 mmol) was added, and the reaction mixture was stirred for an additional 2 h at room temperature. The reaction was quenched by addition of aqueous HCl (50 mL, 2 M) and water (50 mL). The aqueous layer was extracted with ethyl acetate (3 × 75 mL). The combined organic layers were washed with brine and dried with $MgSO_4$, and the solvent was removed in vacuo. The products were purified by column chromatography on silica gel with mixtures of cyclohexane and ethyl acetate. In some cases, addition of aqueous HCl during the workup procedure led to a precipitate, which could be filtered off and recrystallized to give the desired product.

1-(5-Methoxy-2-methylbenzofuran-3-yl)ethanone (12): Yield: 1.00 g, 4.92 mmol, 82%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44 (d, $^4J_{H,H}$ = 2.6 Hz, 1 H, ArH), 7.29 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, ArH), 6.85 (dd, $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.6 Hz, 1 H, ArH), 3.84 (s, 3 H, CH_3), 2.72 (s, 3 H, CH_3), 2.57 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 194.0, 163.3, 156.8, 148.4, 126.8, 117.9, 112.7, 111.2, 104.5, 55.9, 30.9, 15.6 ppm. MS (EI, 70 eV): *m*/*z* (%) = 204 (60) [M^+], 190 (12), 189 (100). HRMS (EI): calcd. for $C_{12}H_{12}O_3$ [M^+] 204.07864; found 204.07900.

1-(5-Methoxy-1,2-dimethyl-1*H*-indol-3-yl)ethanone (13): Yield: 1.03 g, 4.74 mmol, 79%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (d, $^4J_{H,H}$ = 2.4 Hz, 1 H, ArH), 7.14 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, ArH), 6.85 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 2.4 Hz, 1 H, ArH), 3.86 (s, 3 H, CH_3), 3.58 (s, 3 H, CH_3), 2.66 (s, 3 H, CH_3), 2.58 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 194.0, 155.7, 144.9, 131.6, 127.0, 114.0, 111.0, 109.9, 103.8, 55.8, 31.4, 29.5, 12.8 ppm. MS (EI, 70 eV): *m*/*z* (%) = 217 (47) [M^+], 203 (13), 202 (100). HRMS (EI): calcd. for $C_{13}H_{15}NO_2$ [M^+] 217.11028; found 217.10900.

Ethyl 4-(3-Acetyl-2-methylbenzofuran-5-yloxy)butanoate (14): Yield: 1.22 g, 4.02 mmol, 67%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (d, $^4J_{H,H}$ = 2.5 Hz, 1 H, ArH), 7.29 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, ArH), 6.89 (dd, $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.6 Hz, 1 H, ArH), 4.13 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, CH_2), 4.04 (t, $^3J_{H,H}$ = 6.1 Hz, 2 H, CH_2), 2.73 (s, 3 H, CH_3), 2.58 (s, 3 H, CH_3), 2.52 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 2.11 (m, 2 H, CH_2), 1.24 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 194.1, 173.2, 163.3, 156.0, 148.4, 126.8, 117.9, 113.1, 111.2, 105.5, 67.6, 60.4, 31.0, 30.8, 24.7, 15.6, 14.2 ppm. MS (EI, 70 eV): *m*/*z* (%) = 304 (11) [M^+], 217 (14), 175 (39), 115 (94), 87 (100). HRMS (EI): calcd. for $C_{17}H_{20}O_5$ [M^+] 304.13107; found 304.13050.

Ethyl 4-(3-Acetyl-1,2-dimethyl-1*H*-indol-5-yloxy)butanoate (15): Yield:1.24 g, 3.9 mmol, 65%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, ArH), 7.16 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, ArH), 6.87 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 2.3 Hz, 1 H, ArH), 4.17 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, CH_2), 4.09 (t, $^3J_{H,H}$ = 6.2 Hz, 2 H, CH_2), 3.60 (s, 3 H, CH_3), 2.68 (s, 3 H, CH_3), 2.61 (s, 3 H, CH_3), 2.58 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, CH_2), 2.17 (m, 2 H, CH_2), 1.29 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 194.0, 173.3, 155.0, 145.1, 131.8, 127.1, 114.0, 111.5, 110.0, 104.9, 67.5, 60.9, 31.5, 30.9, 29.6, 24.9, 14.3, 12.8 ppm. MS (EI, 70 eV): *m*/*z* (%) = 317 (30) [M^+], 230 (22), 202 (10), 188 (43), 174 (12), 115 (100), 87 (88). HRMS (EI): calcd. for $C_{18}H_{23}NO_4$ [M^+] 317.16271; found 317.16190.

1-[5-(5-Bromopentyloxy)-2-methylbenzofuran-3-yl]ethanone (18): Yield:1.64 g, 4.86 mmol, 81%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (d, $^4J_{H,H}$ = 2.5 Hz, 1 H, ArH), 7.29 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, ArH), 6.85 (dd, $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.6 Hz, 1 H, ArH), 4.00 (t, $^3J_{H,H}$ = 6.3 Hz, 2 H, CH_2), 3.42 (t, $^3J_{H,H}$ = 6.8 Hz, 2 H, CH_2), 2.72 (s, 3 H, CH_3), 2.58 (s, 3 H, CH_3), 1.93 (m, 2 H, CH_2), 1.82 (m, 2 H, CH_2), 1.62 (m, 2 H, CH_2) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 194.0, 163.3, 156.1, 148.4, 126.8, 117.8, 113.1, 111.2, 105.4, 68.4, 33.6, 32.5, 31.0, 28.5, 24.8, 15.6 ppm. MS (EI, 70 eV): *m/z* (%) = 340 (32) [M(^{81}Br)$^+$], 338 (32) [M(^{79}Br)$^+$], 190 (66), 176 (11), 175 (100), 69 (34). HRMS (EI): calcd. for $C_{16}H_{19}O_3Br$ [M$^+$] 338.05176; found 338.04950.

1-[5-(5-Bromopentyloxy)-1,2-dimethyl-1*H*-indol-3-yl]ethanone (19): Yield: 1.62 g, 4.62 mmol, 77%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, ArH), 7.19 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, ArH), 6.87 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 2.3 Hz, 1 H, ArH), 4.04 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, CH_2), 3.66 (s, 3 H, CH_3), 3.43 (t, $^3J_{H,H}$ = 6.8 Hz, 2 H, CH_2), 2.73 (s, 3 H, CH_3), 2.62 (s, 3 H, CH_3), 1.94 (m, 2 H, CH_2), 1.83 (m, 2 H, CH_2), 1.65 (m, 2 H, CH_2) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 194.1, 155.1, 145.0, 131.7, 127.1, 114.0, 111.5, 109.9, 104.9, 68.3, 33.7, 32.5, 31.5, 29.6, 28.6, 24.8, 12.8 ppm. MS (EI, 70 eV): *m/z* (%) = 353 (37) [M(^{81}Br)$^+$], 351 (37) [M(^{79}Br)$^+$], 338 (12), 336 (12), 203 (29), 202 (22), 189 (13), 188 (100), 175 (17), 131 (12), 69 (13). HRMS (EI): calcd. for $C_{17}H_{22}NO_2Br$ [M$^+$] 351.08339; found 351.07860.

1-[5-(Allyloxy)-2-methylbenzofuran-3-yl]ethanone (20): Yield: 1.13 g, 4.92 mmol, 82%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 (d, $^4J_{H,H}$ = 2.5 Hz, 1 H, ArH), 7.29 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, ArH), 6.88 (dd, $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.6 Hz, 1 H, ArH), 6.07 (ddt, $^3J_{H,H}$ = 17.1, $^3J_{H,H}$ = 10.6, $^3J_{H,H}$ = 5.3 Hz, 1 H, CH), 5.43 (dd, $^3J_{H,H}$ = 17.3, $^2J_{H,H}$ = 1.5 Hz, 1 H, CH), 5.28 (dd, $^3J_{H,H}$ = 10.5, $^2J_{H,H}$ = 1.3 Hz, 1 H, CH), 4.57 (dd, $^3J_{H,H}$ = 4.0, $^4J_{H,H}$ = 1.3 Hz, 2 H, CH_2), 2.72 (s, 3 H, CH_3), 2.57 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 194.0, 163.3, 155.7, 148.5, 133.4, 126.8, 117.8, 117.7, 113.3, 111.2, 105.8, 69.7, 30.9, 15.6 ppm. MS (EI, 70 eV): *m/z* (%) = 230 (55) [M$^+$], 215 (10), 189 (54), 147 (52), 69 (11). HRMS (EI): calcd. for $C_{14}H_{14}O_3$ [M$^+$] 230.09429; found 230.09360.

1-[5-(Allyloxy)-1,2-dimethyl-1*H*-indol-3-yl]ethanone (21): Yield: 1.17 g, 4.80 mmol, 80%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, ArH), 7.15 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, ArH), 6.88 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 2.4 Hz 1 H, ArH), 6.09 (ddt, $^3J_{H,H}$ = 22.6, $^3J_{H,H}$ = 10.6, $^3J_{H,H}$ = 5.4 Hz, 1 H, CH), 5.44 (dd, $^3J_{H,H}$ = 17.3, $^2J_{H,H}$ = 1.5 Hz, 1 H, CH), 5.28 (dd, $^3J_{H,H}$ = 10.5, $^2J_{H,H}$ = 1.3 Hz, 1 H, CH), 4.59 (m, 2 H, CH_2), 3.59 (s, 3 H, CH_3), 2.67 (s, 3 H, CH_3), 2.58 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 194.0, 154.7, 145.1, 133.7, 131.8, 127.0, 117.5, 114.0, 111.6, 109.9, 105.2, 69.6, 31.4, 29.5, 12.8 ppm. MS (EI, 70 eV): *m/z* (%) = 243 (39) [M$^+$], 203 (14), 202 (100), 174 (38), 131 (11). HRMS (EI): calcd. for $C_{15}H_{17}NO_2$ [M$^+$] 243.12593; found 243.12510.

1-[2-Methyl-5-(prop-2-ynyloxy)benzofuran-3-yl]ethanone (22): Yield: 1.08 g, 4.74 mmol, 79%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54 (d, $^4J_{H,H}$ = 2.6 Hz, 1 H, ArH), 7.31 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, ArH), 6.92 (dd, $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.6 Hz, 1 H, ArH), 4.72 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H, CH_2), 2.72 (s, 3 H, CH_3), 2.57 (s, 3 H, CH_3), 2.51 (t, $^4J_{H,H}$ = 2.4 Hz, 1 H, CH) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 193.9, 163.5, 154.6, 148.8, 126.8, 117.8, 113.5, 111.3, 106.39, 78.7, 75.5, 56.7, 30.9, 15.6 ppm. MS (EI, 70 eV): *m/z* (%) = 228 (43) [M$^+$], 227 (20), 213 (19), 200 (13), 189 (29), 185 (22), 147 (41). HRMS (EI): calcd. for $C_{14}H_{12}O_3$ [M$^+$] 228.07864; found 228.07770.

1-[1,2-Dimethyl-5-(prop-2-ynyloxy)-1*H*-indol-3-yl]ethanone (23): Yield: 1.10 g, 4.56 mmol, 76%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 (d, $^4J_{H,H}$ = 2.2 Hz, 1 H, ArH), 7.16 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, ArH), 6.91 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 2.2 Hz, 1 H, ArH), 4.73 (d, $^4J_{H,H}$ = 2.1 Hz, 2 H, CH_2), 3.59 (s, 3 H, CH_3), 2.66 (s, 3 H, CH_3), 2.58 (s, 3 H, CH_3), 2.51 (t, $^4J_{H,H}$ = 1.9 Hz, 1 H, CH) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 194.0, 153.6, 145.3, 132.2, 126.9, 114.0, 111.7, 109.9, 105.7, 78.9, 75.3, 56.7, 31.4, 29.5, 12.7 ppm. MS (EI, 70 eV): *m/z* (%) = 241 (50) [M$^+$], 226 (13), 203 (14), 202 (100), 198 (12), 174 (38), 131 (14). HRMS (EI): calcd. for $C_{15}H_{15}NO_2$ [M$^+$] 241.11028; found 241.11000.

1-[5-(4-Bromophenoxy)-2-methylbenzofuran-3-yl]ethanone (24): Yield: 1.53 g, 4.26 mmol, 71%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, $^4J_{H,H}$ = 2.6 Hz, 1 H, ArH), 7.49 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, ArH), 7.32 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, ArH), 7.30 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, ArH) 6.91 (dd, $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.6 Hz, 1 H, ArH), 5.04 (s, 2 H, CH_2), 2.73 (s, 3 H, CH_3), 2.56 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 193.9, 163.4, 155.6, 148.5, 136.0, 131.6, 129.1, 126.9, 121.8, 117.9, 113.4, 111.3, 106.0, 70.0, 30.9, 15.6 ppm. MS (EI, 70 eV): *m/z* (%) = 360 (21) [M(^{81}Br)$^+$], 358 (21) [M(^{79}Br)$^+$], 171 (98), 169 (100), 90 (25), 89 (14). HRMS (EI): calcd. for $C_{18}H_{15}O_3Br$ [M$^+$] 358.02046; found 358.02010.

1-[5-(4-Bromobenzyloxy)-1,2-dimethyl-1*H*-indol-3-yl]ethanone (25): Yield:1.47 g, 3.96 mmol, 66%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H, ArH), 7.48 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, ArH), 7.32 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, ArH), 7.16 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, ArH), 6.91 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 2.3 Hz, 1 H, ArH), 5.06 (s, 2 H, CH_2), 3.61 (s, 3 H, CH_3), 2.68 (s, 3 H, CH_3), 2.57 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 194.0, 154.6, 145.1, 136.4, 131.9, 131.6, 129.1, 127.0, 121.66, 114.1, 111.8, 110.0, 105.4, 70.0, 31.4, 29.6, 12.8 ppm. MS (EI, 70 eV): *m/z* (%) = 373 (17) [M(^{81}Br)$^+$], 371 (17) [M(^{79}Br)$^+$], 203 (15), 202 (100), 174 (22). HRMS (EI): calcd. for $C_{19}H_{18}NO_2Br$ [M$^+$] 371.05209; found 371.04990.

1-[5-(Anthracen-9-yloxy)-2-methylbenzofuran-3-yl]ethanone (26): Yield: 1.87 g, 4.92 mmol, 82%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.51 (s, 1 H, ArH), 8.31 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, ArH), 8.03 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, ArH), 7.77 (d, $^4J_{H,H}$ = 2.5 Hz, 1 H, ArH), 7.54 (m, 2 H, ArH), 7.47 (m, 2 H, ArH), 7.37 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H, ArH), 7.04 (dd, $^3J_{H,H}$ = 9.1, $^4J_{H,H}$ = 2.5 Hz, 1 H, ArH), 6.03 (s, 2 H, CH_2), 2.77 (s, 3 H, CH_3), 2.58 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 194.2, 163.5, 156.5, 148.7, 131.5, 131.0, 129.2, 129.0, 127.0, 126.9, 126.6, 125.1, 124.1, 118.0, 113.6, 111.5, 105.9, 63.6, 31.1, 15.7 ppm. MS (EI, 70 eV): *m/z* (%) = 380 (4) [M$^+$], 192 (19), 191 (100), 189 (15), 178 (13). HRMS (EI): calcd. for $C_{26}H_{20}O_3$ [M$^+$] 380.14124; found 380.13820.

1-[5-(Anthracen-9-ylmethoxy)-1,2-dimethyl-1*H*-indol-3-yl]ethanone (27): Yield: 1.65 g, 4.20 mmol, 70%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.51 (s, 1 H, ArH), 8.34 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H, ArH), 8.03 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, ArH), 7.82 (d, $^4J_{H,H}$ = 2.4 Hz, 1 H, ArH), 7.52 (m, 2 H, ArH), 7.48 (m, 2 H, ArH), 7.25 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, ArH), 7.05 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 2.4 Hz, 1 H, ArH), 6.05 (s, 2 H, CH_2), 3.69 (s, 3 H, CH_3) 2.76 (s, 3 H, CH_3), 2.61 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 194.2, 155.4, 145.1, 131.9, 131.4, 130.9, 129.0, 128.7, 127.3, 127.1, 126.4, 125.0, 124.1, 114.1, 111.9, 110.1, 105.2, 63.5, 31.5, 29.5, 12.8 ppm. MS (EI, 70 eV): *m/z* (%) = 394 (13), 393 (43) [M$^+$], 216 (13), 215 (78), 203 (14), 192 (19), 191 (75), 189 (20), 188 (32), 187 (15), 179 (16), 178 (100). HRMS (EI): calcd. for $C_{27}H_{23}NO_2$ [M$^+$] 393.17288; found 393.17330.

1-(6-Bromo-5-methoxy-2-methylbenzofuran-3-yl)ethanone (28): Yield: 1.29 g, 4.56 mmol, 76%. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.84 (s, 1 H, ArH), 7.51 (s, 1 H, ArH), 3.87 (s, 3 H, CH_3), 2.72 (s, 3 H, CH_3), 2.56 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, [D$_6$]-

DMSO): δ = 193.6, 163.7, 152.5, 147.0, 126.1, 117.1, 115.1, 107.6, 103.5, 56.5, 30.8, 15.4 ppm. MS (EI, 70 eV): *m*/*z* (%) = 285 (12), 284 (90) [M(^{81}Br)$^+$], 283 (19), 282 (92) [M(^{79}Br)$^+$], 270 (12), 269 (97), 268 (13), 267 (100). HRMS (EI): calcd. for $C_{12}H_{11}O_3Br$ [M$^+$] 281.98916; found 281.98900.

1-(6-Bromo-5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)ethanone (29): Yield: 1.49 g, 5.04 mmol, 84%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.56 (s, 1 H, ArH), 7.40 (s, 1 H, ArH), 3.92 (s, 3 H, CH_3), 3.57 (s, 3 H, CH_3), 2.65 (s, 3 H, CH_3), 2.55 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 193.7, 151.7, 144.8, 131.8, 126.3, 114.2, 113.7, 106.8, 103.5, 56.7, 31.3, 29.8, 12.9 ppm. MS (EI, 70 eV): *m*/*z* (%) = 297 (66) [M(^{81}Br)$^+$], 295 (67) [M(^{79}Br)$^+$], 283 (13), 282 (98), 281 (14), 280 (100), 267 (12), 265 (12), 173 (17), 130 (17). HRMS (EI): calcd. for $C_{13}H_{14}NO_2Br$ [M$^+$] 295.02079; found 295.01880.

General Preparation of Fulgides:[11] A solution of diethyl isopropylidenesuccinate[12] (15 mmol) in dry THF (15 mL) was cooled to –78 °C, and LDA (7.5 mL, 15 mmol; 2 M, THF/*n*-heptane/ethylbenzene) was added under argon. After stirring for 1 h, the appropriate ketone (10 mmol) dissolved in THF (30 mL) was added via syringe. The reaction mixture was warmed to room temperature overnight and stirred for an additional 24 h. The reaction progress was monitored by TLC. The reaction mixture was acidified with aqueous HCl (2 M), and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with saturated aqueous NaCl solution, dried with $MgSO_4$, and the solvent was removed in vacuo. The residue was dissolved in cyclohexane/ethyl acetate (7:3), filtered through silica gel, and the solvent was removed in vacuo again. The residue was dissolved in ethanol (60 mL), and a saturated aqueous solution of KOH (5 mL) was added. After stirring for 20 h at 70 °C, the reaction mixture was poured onto ice and acidified with aqueous HCl (2 M). The aqueous layer was extracted with ethyl acetate (3 × 50 mL), and the combined organic layers were washed with saturated aqueous NaCl, dried with $MgSO_4$, and the solvent was removed in vacuo. The dark brown residue was dissolved in dichloromethane (50 mL), and *N*,*N*′-dicyclohexylcarbodiimide (DCC) (4.13 g, 20 mmol) was added. After stirring for 48 h, the reaction mixture was filtered through silica gel, and the solvent was removed in vacuo. The products were purified by column chromatography with mixtures of cyclohexane and ethyl acetate as eluent. Benzofuryl fulgides were recrystallized from cyclohexane or diethyl ether and indolyl fulgides were recrystallized from 2-propanol.

(*E*)-3-[1-(5-Methoxy-2-methylbenzofuran-3-yl)ethylidene]-4-(propan-2-ylidene)dihydrofuran-2,5-dione (30): Yield: 325 mg, 1.0 mmol, 7%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29 (d, $^3J_{H,H}$ = 9.4 Hz, 1 H, ArH), 6.85 (dd, $^3J_{H,H}$ = 9.4, $^4J_{H,H}$ = 2.5 Hz, 1 H, ArH), 6.70 (d, $^4J_{H,H}$ = 2.5 Hz, 1 H, ArH), 3.79 (s, 3 H, CH_3), 2.72 (s, 3 H, CH_3), 2.23 (s, 6 H, CH_3), 1.12 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.6, 163.0, 156.2, 155.5, 153.5, 148.9, 145.0, 126.5, 121.5, 120.8, 119.6, 112.9, 111.6, 102.8, 55.9, 26.7, 22.7, 22.0, 14.0 ppm. MS (EI, 70 eV): *m*/*z* (%) = 327 (22), 326 (100) [M$^+$], 311 (43), 309 (12), 283 (20), 281 (12), 267 (41), 265 (15), 253 (13), 239 (17), 223 (11), 204 (11), 165 (11), 162 (21), 152 (12), 115 (13), 106 (12), 91 (12), 77 (10). HRMS (ESI): calcd. for $C_{19}H_{18}O_5Na^+$ 349.10464; found 349.10480; calcd. for $(C_{19}H_{18}O_5)_2Na^+$ 675.22026; found 675.22007.

(*E*)-3-[1-(5-Methoxy-1,2-dimethyl-1*H*-indol-3-yl)ethylidene]-4-(propan-2-ylidene)dihydrofuran-2,5-dione (31): Yield: 305 mg, 0.9 mmol, 9%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.16 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, ArH), 6.84 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 2.4 Hz, 1 H, ArH), 6.71 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, ArH), 3.78 (s, 3 H, CH_3), 3.65 (s, 3 H, CH_3), 2.77 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 2.17 (s, 3 H, CH_3), 0.92 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.1, 163.8, 154.7, 153.1, 149.4, 136.1, 132.0, 125.0, 121.5, 118.4, 116.4, 111.7, 110.0, 101.8, 55.7, 30.0, 26.2, 23.6, 22.6, 12.3 ppm. MS (EI, 70 eV): *m*/*z* (%) = 340 (22), 339 (100) [M$^+$], 324 (14), 296 (23), 294 (13), 280 (13), 266 (37), 252 (30), 240 (12), 200 (20), 175 (53). HRMS (EI): calcd. for $C_{20}H_{21}NO_4$ [M$^+$] 339.14706; found 339.14500.

(*E*)-4-(3-{1-[2,5-Dioxo-4-(propan-2-ylidene)dihydrofuran-3(2*H*)-ylidene]ethyl}-2-methylbenzofuran-5-yloxy)butanoic Acid (32): Yield: 239 mg, 0.6 mmol, 6%. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 12.13 (s, 1 H, COOH), 7.41 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, ArH), 7.01 (d, $^4J_{H,H}$ = 2.5 Hz, 1 H, ArH), 6.86 (dd, $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.5 Hz, 1 H, ArH), 3.97 (m, 2 H, CH_2), 2.67 (s, 3 H, CH_3), 2.37 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, CH_3), 2.24 (s, 3 H, CH_3), 2.15 (s, 3 H, CH_3), 1.92 (p, $^3J_{H,H}$ = 6.7 Hz, 2 H, CH_2), 1.05 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 174.1, 163.5, 162.9, 155.0, 154.7, 153.7, 148.1, 144.1, 126.4, 121.2, 120.5, 119.2, 113.1, 111.4, 104.0,67.2, 30.1, 26.1, 24.2, 22.1, 21.7, 13.6 ppm. MS (EI, 70 eV): *m*/*z* (%) = 399 (26), 398 (100) [M$^+$], 383 (24), 381 (45), 339 (26), 312 (73), 311 (23), 297 (71), 295 (46), 269 (30), 268 (22), 267 (33), 253 (32), 251 (22), 239 (24), 225 (37), 232 (25), 165 (25), 152 (23), 148 (31). HRMS (EI): calcd. for $C_{22}H_{22}O_7$ [M$^+$] 398.13655; found 398.13500.

(*E*)-4-(3-{1-[2,5-Dioxo-4-(propan-2-ylidene)dihydrofuran-3(2*H*)-ylidene]ethyl}-1,2-dimethyl-1*H*-indol-5-yloxy)butanoic Acid (33): Yield: 288 mg, 0.7 mmol, 7%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.15 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, ArH), 6.83 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 2.3 Hz, 1 H, ArH), 6.74 (d, $^4J_{H,H}$ = 2.2 Hz, 1 H, ArH), 3.99 (m, 2 H, CH_2), 3.64 (s, 3 H, CH_3), 2.77 (s, 3 H, CH_3), 2.59 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_3), 2.19 (s, 3 H, CH_3), 2.17 (s, 3 H, CH_3), 2.11 (m, 2 H, CH_2), 0.92 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, [D$_6$]-DMSO): δ = 174.2, 163.9, 163.5, 153.3, 152.3, 149.1, 137.4, 131.8, 124.8, 121.2, 117.4, 115.5, 111.4, 110.6, 102.7, 67.0, 30.2, 29.9, 25.7, 24.4, 23.4, 22.1, 12.0 ppm. MS (EI, 70 eV): *m*/*z* (%) = 412 (24), 411 (81) [M$^+$], 394 (16), 352 (19), 325 (35), 324 (20), 321 (21), 308 (20), 307 (18), 282 (19), 280 (18), 266 (24), 264 (20), 252 (28), 238 (24), 161 (50). HRMS (EI): calcd. for $C_{23}H_{25}NO_6$ [M$^+$] 411.16819; found 411.16740.

(*E*)-3-{1-[5-(5-Ethoxypentyloxy)-2-methylbenzofuran-3-yl]ethylidene}-4-(propan-2-ylidene)dihydrofuran-2,5-dione (34): Yield: 213 mg, 0.5 mmol, 5%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, ArH), 6.84 (dd, $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.5 Hz, 1 H, ArH), 6.71 (d, $^4J_{H,H}$ = 2.5 Hz, 1 H, ArH), 3.92 (m, 2 H, CH_2), 3.45 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, CH_2), 3.42 (t, $^3J_{H,H}$ = 6.5 Hz, 2 H, CH_2), 2.72 (s, 3 H, CH_3), 2.23 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 1.80 (m, 2 H, CH_2), 1.64 (m, 2 H, CH_2), 1.53 (m, 2 H, CH_2), 1.18 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.12 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.5, 162.9, 155.7, 155.4, 153.2, 148.8, 145.1, 126.5, 121.4, 120.7, 119.5, 113.2, 111.5, 103.6, 70.5, 68.6, 66.1, 29.5, 29.2, 26.7, 22.8, 22.7, 21.9, 15.2, 14.0 ppm. MS (EI, 70 eV): *m*/*z* (%) = 426 (31) [M$^+$], 297 (12), 115 (100), 69 (66). HRMS (EI): calcd. for $C_{25}H_{30}O_6$ [M$^+$] 426.20424; found 426.20280.

(*E*)-3-{1-[5-(5-Ethoxypentyloxy)-1,2-dimethyl-1*H*-indol-3-yl]ethylidene}-4-(propan-2-ylidene)dihydrofuran-2,5-dione (35): Yield: 351 mg, 0.8 mmol, 8%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.15 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, ArH), 6.84 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 2.4 Hz, 1 H, ArH), 6.74 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, ArH), 3.93 (m, 2 H, CH_2), 3.63 (s, 3 H, CH_3), 3.45 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, CH_2), 3.43 (t, $^3J_{H,H}$ = 6.6 Hz, 2 H, CH_2), 2.77 (s, 3 H, CH_3), 2.18 (s, 6 H, CH_3), 1.80 (m, 2 H, CH_2), 1.64 (m, 2 H, CH_2), 1.52 (m, 2 H, CH_2), 1.18 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 0.92 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.1, 163.8, 154.2, 152.9, 149.5, 135.9,

132.0, 125.2, 121.6, 118.5, 116.4, 112.2, 109.9, 102.9, 70.5, 68.5, 66.1, 30.0, 29.6, 29.3, 26.2, 23.6, 22.8, 22.7, 15.2, 12.2 ppm. MS (EI, 70 eV): *m/z* (%) = 440 (29), 439 (100) [M^+], 252 (17), 161 (14), 115 (53), 69 (38), 59 (28). HRMS (EI): calcd. for $C_{26}H_{33}NO_5$ [M^+] 439.23587; found 439.23450.

(*E*)-3-{1-[5-(Allyloxy)-2-methylbenzofuran-3-yl]ethylidene}-4-(propan-2-ylidene)dihydrofuran-2,5-dione (36): Yield: 387 mg, 1.1 mmol, 11%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, ArH), 6.88 (dd, $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.5 Hz, 1 H, ArH), 6.75 (d, $^4J_{H,H}$ = 2.5 Hz, 1 H, ArH), 6.04 (ddt, $^3J_{H,H}$ = 17.2, $^3J_{H,H}$ = 10.5, $^3J_{H,H}$ = 5.3 Hz, 1 H, CH), 5.40 (ddd, $^3J_{H,H}$ = 17.3, $^4J_{H,H}$ = 3.1, $^2J_{H,H}$ = 1.5 Hz, 1 H, CH), 5.28 (dd, $^3J_{H,H}$ = 10.5, $^2J_{H,H}$ = 1.4 Hz, 1 H, CH), 4.51 (m, 2 H, CH_2), 2.72 (s, 3 H, CH_3), 2.23 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3), 1.13 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.5, 162.9, 155.5, 155.2, 153.3, 149.0, 145.0, 133.2, 126.5, 121.5, 120.7, 119.5, 117.8, 113.5, 111.6, 104.0, 69.7, 26.7, 22.7, 22.0, 14.0 ppm. MS (EI, 70 eV): *m/z* (%) = 353 (23), 352 (100) [M^+], 337 (15), 312 (13), 311 (61), 293 (20), 283 (22), 268 (13), 267 (56), 265 (12), 239 (16), 165 (13), 152 (13), 115 (11). HRMS (EI): calcd. for $C_{21}H_{20}O_5$ [M^+] 352.13107; found 352.12900.

(*E*)-3-{1-[5-(Allyloxy)-1,2-dimethyl-1*H*-indol-3-yl]ethylidene}-4-(propan-2-ylidene)dihydrofuran-2,5-dione (37): Yield: 292 mg, 0.8 mmol, 8%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.16 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, ArH), 6.88 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 2.4 Hz, 1 H, ArH), 6.77 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, ArH), 6.06 (ddt, $^3J_{H,H}$ = 17.1, $^3J_{H,H}$ = 10.5, $^3J_{H,H}$ = 5.3 Hz, 1 H, CH), 5.41 (dd, $^3J_{H,H}$ = 17.3, $^2J_{H,H}$ = 1.6 Hz, 1 H, CH), 5.26 (dd, $^3J_{H,H}$ = 10.5, $^2J_{H,H}$ = 1.4 Hz, 1 H, CH), 4.51 (d, $^3J_{H,H}$ = 5.2 Hz, 2 H, ArH), 3.64 (s, 3 H, CH_3), 2.77 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.2, 163.8, 153.8, 153.1, 149.4, 136.0, 133.6, 132.2, 125.2, 121.5, 118.6, 117.5, 116.4, 112.3, 110.0, 103.3, 69.6, 30.0, 26.2, 23.6, 22.7, 12.3 ppm. MS (EI, 70 eV): *m/z* (%) = 366 (25), 365 (100) [M^+], 324 (51), 296 (26), 280 (17), 278 (16), 252 (62), 226 (17), 208 (16). HRMS (EI): calcd. for $C_{22}H_{23}NO_4$ [M^+] 365.16271; found 365.16080.

(*E*)-3-{1-[1,2-Dimethyl-5-(prop-2-ynyloxy)-1*H*-indol-3-yl]ethylidene}-4-(propan-2-ylidene)dihydrofuran-2,5-dione (39): Yield: 254 mg, 0.7 mmol, 7%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.18 (m, 1 H, ArH), 6.91 (m, 2 H, ArH), 4.66 (d, $^4J_{H,H}$ = 2.3 Hz, 2 H, CH_2), 3.65 (s, 3 H, CH_3), 2.77 (s, 3 H, CH_3), 2.51 (t, $^3J_{H,H}$ = 2.3 Hz, 1 H, CH), 2.18 (s, 3 H, CH_3), 0.93 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.1, 163.8, 153.2, 152.8, 149.3, 136.1, 132.6, 125.1, 121.5, 118.8, 116.5, 112.4, 110.0, 104.0, 78.8, 75.5, 56.9, 30.0, 26.3, 23.6, 22.7, 12.3 ppm. MS (EI, 70 eV): *m/z* (%) = 364 (25), 363 (100) [M^+], 324 (28), 320 (13), 296 (16), 276 (13), 252 (39), 224 (18), 208 (13), 199 (17). HRMS (EI): calcd. for $C_{22}H_{21}NO_4$ [M^+] 363.14706; found 363.14580.

(*E*)-3-{1-[5-(4-Bromobenzyloxy)-2-methylbenzofuran-3-yl]ethylidene}-4-(propan-2-ylidene)dihydrofuran-2,5-dione (40): Yield: 624 mg, 1.3 mmol, 13%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, ArH), 7.30 (m, 3 H, ArH), 6.92 (dd, $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.5 Hz, 1 H, ArH), 6.78 (d, $^4J_{H,H}$ = 2.5 Hz, 1 H, ArH), 4.99 (s, 2 H, CH_2), 2.70 (s, 3 H, CH_3), 2.23 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.5, 162.9, 155.5, 155.0, 153.5, 149.1, 144.8, 135.2, 131.7, 129.1, 126.5, 121.9, 121.5, 120.7, 119.5, 113.5, 111.7, 104.3, 70.1, 26.7, 22.7, 21.9, 14.0 ppm. MS (EI, 70 eV): *m/z* (%) = 482 (18) [$M(^{81}Br)^+$], 480 (18) [$M(^{79}Br)^+$], 311 (20), 267 (15), 171 (97), 169 (100), 90 (22), 89 (12). HRMS (EI): calcd. for $C_{25}H_{21}O_5Br$ [M^+] 480.05724; found 480.05550.

(*E*)-3-{1-[5-(4-Bromobenzyloxy)-1,2-dimethyl-1*H*-indol-3-yl]ethylidene}-4-(propan-2-ylidene)dihydrofuran-2,5-dione (41): Yield: 740 mg, 1.5 mmol, 15%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, ArH), 7.31 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, ArH), 7.17 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, ArH), 6.91 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 2.3 Hz, 1 H, ArH), 6.80 (d, $^4J_{H,H}$ = 2.2 Hz, 1 H, ArH), 4.99 (s, 2 H, CH_2), 3.64 (s, 3 H, CH_3), 2.75 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 0.92 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.1, 163.8, 153.6, 153.0, 149.3, 136.3, 136.1, 132.3, 131.6, 129.1, 125.1, 121.7, 121.6, 118.7, 116.4, 112.4, 110.1, 103.6, 70.0, 30.0, 26.2, 23.6, 22.7, 12.3 ppm. MS (EI, 70 eV): *m/z* (%) = 495 (32) [$M(^{81}Br)^+$], 493 (32) [$M(^{79}Br)^+$], 325 (23), 324 (100), 306 (11), 296 (24), 280 (22), 278 (11), 253 (16), 252 (75), 236 (10), 208 (12), 171 (17), 169 (18). HRMS (EI): calcd. for $C_{26}H_{24}NO_4Br$ [M^+] 493.08887; found 493.08740.

(*E*)-3-{1-[5-(Anthracen-9-ylmethoxy)-2-methylbenzofuran-3-yl]ethylidene}-4-(propan-2-ylidene)dihydrofuran-2,5-dione (42): Yield: 502 mg, 1.0 mmol, 10%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.50 (s, 1 H, ArH), 8.28 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, ArH), 8.02 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, ArH), 7.53 (m, 2 H, ArH), 7.47 (m, 2 H, ArH), 7.34 (d, $^3J_{H,H}$ = 9.6 Hz, 1 H, ArH), 7.04 (dd, $^3J_{H,H}$ = 6.4, $^4J_{H,H}$ = 2.5 Hz 2 H, ArH), 5.96 (s, 2 H, CH_2), 2.69 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 1.16 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.2, 160.9, 157.2, 155.6, 154.4, 149.2, 143.7, 131.4, 130.9, 129.1, 128.9, 127.8, 127.0, 126.5, 125.0, 124.0, 122.8, 121.3, 114.9, 112.5, 111.7, 104.5, 63.7, 27.2, 24.0, 22.4, 13.6 ppm. MS (EI, 70 eV): *m/z* (%) = 502 (12) [M^+], 192 (28), 191 (62), 189 (12), 179 (17), 178 (100). HRMS (EI): calcd. for $C_{33}H_{26}O_5$ [M^+] 502.17802; found 502.17650.

(*E*)-3-{1-[5-(Anthracen-9-ylmethoxy)-1,2-dimethyl-1*H*-indol-3-yl]-ethylidene}-4-(propan-2-ylidene)dihydrofuran-2,5-dione (43): Yield: 412 mg, 0.8 mmol, 8%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.49 (s, 1 H, ArH), 8.32 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, ArH), 8.02 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, ArH), 7.51 (m, 2 H, ArH), 7.46 (m, 2 H, ArH), 7.20 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, ArH), 7.11 (d, $^4J_{H,H}$ = 2.2 Hz, 1 H, ArH), 6.99 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 2.3 Hz, 1 H, ArH), 5.97 (d, $^2J_{H,H}$ = 10.8 Hz, 1 H, CH_2), 5.94 (d, $^2J_{H,H}$ = 10.8 Hz, 1 H, CH_2), 3.64 (s, 3 H, CH_3), 2.78 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.1, 163.8, 154.3, 153.0, 149.5, 136.0, 132.4, 131.4, 131.0, 129.0, 128.8, 127.2, 126.4, 125.2, 125.0, 124.0, 121.6, 118.5, 116.5, 112.7, 110.1, 103.6, 63.6, 30.0, 26.3, 23.5, 22.7, 12.3 ppm. MS (EI, 70 eV): *m/z* (%) = 515 (11) [M^+], 325 (22), 252 (11), 192 (47), 191 (100), 189 (21), 178 (44). HRMS (EI): calcd. for $C_{34}H_{29}NO_4$ [M^+] 515.20966; found 515.21080.

(*E*)-3-[1-(6-Bromo-5-methoxy-2-methylbenzofuran-3-yl)ethylidene]-4-(propan-2-ylidene)dihydrofuran-2,5-dione (44): Yield:285 mg, 0.7 mmol, 7%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.61 (s, 1 H, ArH), 6.65 (s, 1 H, ArH), 3.86 (s, 3 H, CH_3), 2.72 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.4, 162.8, 155.8, 154.2, 152.5, 148.4, 144.0, 125.5, 121.9, 120.7, 119.5, 115.9, 108.7, 101.8, 56.8, 26.6, 22.7, 22.0, 14.1 ppm. MS (EI, 70 eV): *m/z* (%) = 407 (20), 406 (100), 405 (22), 404 (100), 391 (26), 389 (34), 363 (16), 361 (22), 347 (32), 345 (40), 310 (17), 165 (22), 152 (17). HRMS (EI): calcd. for $C_{19}H_{17}O_5Br$ [M^+] 404.02594; found 404.02450.

(*E*)-3-[1-(6-Bromo-5-methoxy-1,2-dimethyl-1*H*-indol-3-yl)ethylidene]-4-(propan-2-ylidene)dihydrofuran-2,5-dione (45): Yield: 375 mg, 0.9 mmol, 9%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47 (s, 1 H, ArH), 6.66 (s, 1 H, ArH), 3.84 (s, 3 H, CH_3), 3.63 (s, 3 H, CH_3), 2.75 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 2.16 (s, 3 H, CH_3), 0.91 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.0,

163.6, 153.5, 150.7, 148.4, 136.7, 132.0, 124.0, 121.4, 119.1, 116.4, 113.9, 107.0, 101.7, 56.6, 30.1, 26.1, 23.7, 22.6, 12.3 ppm. MS (EI, 70 eV): *m/z* (%) = 420 (23), 419 (100) [M(^{81}Br)$^+$], 418 (24), 417 (100) [M(^{79}Br)$^+$], 402 (23), 376 (20), 374 (33), 346 (27), 344 (24), 332 (28), 330 (31), 321 (24), 280 (24), 278 (24), 265 (26), 255 (45), 253 (47). HRMS (EI): calcd. for $C_{20}H_{20}NO_4Br$ [M$^+$] 417.05757; found 417.05740.

(*E*)-3-[1-(5-{[1-(Anthracen-9-ylmethyl)-1*H*-1,2,3-triazol-4-yl]methoxy}-1,2-dimethyl-1*H*-indol-3-yl)ethylidene]-4-(propan-2-ylidene)-dihydrofuran-2,5-dione (48): Alkyne indolyl fulgide **39** (53 mg, 0.15 mmol) was dissolved in chloroform (20 mL), and **46** (75 mg, 0.31 mmol) and [Cu(PPh$_3$)$_3$Br] (20 mg, 0.02 mmol) were added. After stirring for 20 h at room temperature the solvent was removed in vacuo, and the residue was purified by column chromatography to give **48** as a yellow solid. Yield: 46 mg, 0.07 mmol, 48%. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.73 (s, 1 H, ArH), 8.60 (d, ^{3}($_{H,H}$ = 8.7 Hz, 2 H, ArH), 8.15 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, ArH), 7.63 (m, 2 H, ArH), 7.56 (m, 2 H, ArH), 7.30 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, ArH), 6.92 (d, $^4J_{H,H}$ = 2.2 Hz, 1 H, ArH), 6.74 (dd, $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.3 Hz, 1 H, ArH),6.64 (m, 2 H, CH$_2$), 5.75 (s, 1 H, CH), 5.03 (d, $^2J_{H,H}$ = 11.9 Hz, 1 H, CH$_2$), 4.92 (d, $^2J_{H,H}$ = 11.9 Hz, 1 H, CH$_2$), 3.62 (s, 3 H, CH$_3$), 2.62 (s, 3 H, CH$_3$), 2.13 (s, 3 H, CH$_3$), 2.09 (s, 3 H, CH$_3$), 0.76 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 164.3, 164.0, 153.3, 152.7, 149.5, 143.4, 137.7, 132.4, 131.5, 130.8, 129.6, 127.6, 126.2, 125.9, 125.3, 124.5, 124.5, 121.6, 117.8, 115.9, 111.9, 111.0, 103.5, 55.4, 46.0, 30.3, 26.1, 26.0, 23.6, 22.6, 12.5 ppm. MS (ESI): *m/z* = 619 [M – H + Na$^+$]. HRMS (EI): calcd. for $C_{37}H_{33}N_4O_4^+$ 597.24963; found 597.24967; calcd for $C_{37}H_{32}N_4O_4Na^+$ 619.23158; found 619.23168.

(*E*)-3-{1-[5-({1-[(7-Methoxy-2-oxo-2*H*-chromen-4-yl)methyl]-1*H*-1,2,3-triazol-4-yl}methoxy)-1,2-dimethyl-1*H*-indol-3-yl]ethylidene}-4-(propan-2-ylidene)dihydrofuran-2,5-dione (49): Alkyne indolyl fulgide **39** (53 mg, 0.15 mmol) was dissolved in chloroform (20 mL), and **47** (58 mg, 0.25 mmol) and [Cu(PPh$_3$)$_3$Br] (20 mg, 0.02 mmol) were added. After stirring for 25 h at room temperature the solvent was removed in vacuo, and the residue was purified by column chromatography to give **49** as a yellow solid. Yield: 50 mg, 0.09 mmol, 60%. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.72 (s, 1 H, ArH), 7.56 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, ArH), 7.20 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, ArH), 6.88 (m, 1 H, ArH), 6.87 (s, 1 H, CH), 6.88 (dd, $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.3 Hz, 1 H, ArH), 6.83 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, ArH), 5.79 (s, 1 H, CH), 5.66 (s, 2 H, CH$_2$), 5.21 (d, $^2J_{H,H}$ = 12.3 Hz, 1 H, CH$_2$), 5.18 (d, $^2J_{H,H}$ = 12.3 Hz, 1 H, CH$_2$) 3.83 (s, 3 H, CH$_3$), 3.62 (s, 3 H, CH$_3$), 2.71 (s, 3 H, CH$_3$), 2.15 (s, 3 H, CH$_3$), 2.14 (s, 3 H, CH$_3$), 0.89 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (126 MHz, CDCl$_3$): δ = 164.0, 163.8, 163.2, 160.2, 155.6, 153.3, 153.1, 149.4, 148.1, 145.4, 136.2, 132.6, 125.2, 124.6, 123.3, 121.4, 118.5, 116.3, 112.9, 112.0, 111.7, 110.4, 110.1, 104.1, 101.3, 62.9, 55.8, 50.2, 30.0, 26.2, 23.4, 22.6, 12.2 ppm. MS (ESI): *m/z* = 617 [M – H + Na$^+$]. HRMS (ESI): calcd. for $C_{33}H_{31}N_4O_7^+$ 595.21873; found 595.21843; calcd. for $C_{33}H_{30}N_4O_7Na^+$ 617.20067; found 617.20040.

Supporting Information (see footnote on the first page of this article): UV/Vis and emission spectra of conjugates **42**/**43** and **48**/**49**.

Acknowledgments

This work was supported by the Biophotonics Initiative of the German Ministry of Research and Education (BMBF) (grants 13N9234).

[1] a) B. L. Feringa, *Molecular switches*, Wiley-VCH, Weinheim, **2003**; b) H. Dürr, H. Bouas-Laurent, *Photochromism*: *Molecules and Systems*, Elsevier, Amsterdam, **2006**.

[2] a) A. S. Dvornikov, E. P. Walker, P. M. Rentzepis, *J. Phys. Chem. A* **2009**, *113*, 13633–13644; b) Y. Chen, T. Li, M. Fan, X. Mai, H. Zhao, D. Xu, *Mater. Sci. Eng. B* **2005**, *123*, 53–56; c) S. Kawata, Y. Kawata, *Chem. Rev.* **2000**, *100*, 1777–1788.

[3] a) J. Fölling, S. Polyakova, V. Belov, A. van Blaaderen, M. L. Bossi, S. W. Hell, *Small* **2008**, *4*, 134–142; b) F. M. Raymo, M. Tomasulo, *Chem. Soc. Rev.* **2005**, *34*, 327.

[4] a) H. Mizuno, P. Dedecker, R. Ando, T. Fukano, J. Hofkens, A. Miyawaki, *Photochem. Photobiol. Sci.* **2010**, *9*, 239; b) J. Cusido, E. Deniz, F. M. Raymo, *Eur. J. Org. Chem.* **2009**, 2031–2045.

[5] a) S. Malkmus, F. O. Koller, S. Draxler, T. E. Schrader, W. J. Schreier, T. Brust, J. A. DiGirolamo, W. J. Lees, W. Zinth, M. Braun, *Adv. Funct. Mater.* **2007**, *17*, 3657–3662; b) B. Yao, Y. Wang, N. Menke, M. Lei, Y. Zheng, L. Ren, G. Chen, Y. Chen, M. Fan, *Mol. Cryst. Liq. Cryst.* **2005**, *430*, 211–219; c) Y. Yokoyama, *Chem. Rev.* **2000**, *100*, 1717–1740.

[6] V. A. Barachevsky, Y. P. Strokach, Y. A. Puankov, M. M. Krayushkin, *J. Phys. Org. Chem.* **2007**, *20*, 1007–1020.

[7] a) A. P. Glaze, H. G. Heller, J. Whittall, *J. Chem. Soc. Perkin Trans. 2* **1992**, 591–594; b) P. J. Darcy, H. G. Heller, P. J. Strydom, J. Whittall, *J. Chem. Soc. Perkin Trans. 1* **1981**, 202–205.

[8] Y. Liang, A. S. Dvornikov, P. M. Rentzepis, *Macromolecules* **2002**, *35*, 9377–9382.

[9] S. Nithyanandan, P. Kannan, K. Senthil Kumar, P. Ramamurthy, *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 1138–1146.

[10] T. I. Mukhanova, L. M. Alekseeva, E. F. Kuleshova, Y. N. Sheinker, V. G. Granik, *Pharm. Chem. J.* **1993**, *27*, 136–142.

[11] C. J. Thomas, M. A. Wolak, R. R. Birge, W. J. Lees, *J. Org. Chem.* **2001**, *66*, 1914–1918.

[12] C. G. Overberger, C. W. Roberts, *J. Am. Chem. Soc.* **1949**, *71*, 3618–3621.

[13] Yield over three steps. Isolation and purification of intermediate products results in no higher yields. In this study only the (*E*)-isomers were isolated and investigated.

[14] S. Zarwell, S. Dietrich, C. Schulz, P. Dietrich, F. Michalik, K. Rück-Braun, *Eur. J. Org. Chem.* **2009**, 2088–2095.

[15] a) V. D. Bock, H. Hiemstra, J. H. van Maarseveen, *Eur. J. Org. Chem.* **2006**, 51–68; b) H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021; c) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2002**, *41*, 2596–2599.

[16] O. Tosic, J. Mattay, *Eur. J. Org. Chem.* **2011**, 371–376.

[17] D. E. Stack, A. L. Hill, C. B. Diffendaffer, N. M. Burns, *Org. Lett.* **2002**, *4*, 4487–4490.

[18] a) J. A. Findlay, P. Mebe, *Can. J. Chem.* **1980**, *58*, 1427–1434; b) A. M. Jawalekar, N. Meeuwenoord, J. G. O. Cremers, H. S. Overkleeft, G. A. van der Marel, F. P. J. T. Rutjes, F. L. van Delft, *J. Org. Chem.* **2008**, *73*, 287–290.

[19] R. Gujadhur, D. Venkataraman, J. Kintigh, *Tetrahedron Lett.* **2001**, *42*, 4791–4793.

[20] a) T. Förster, *Ann. Phys.* **1948**, *437*, 55–75; b) T. Förster, *Discuss. Faraday Soc.* **1959**, *27*, 7–17.

[21] F. Strübe, R. Siewertsen, F. D. Sönnichsen, F. Renth, F. Temps, J. Mattay, *Eur. J. Org. Chem.* **2011**, 1947–1955.

[22] a) S. Uchida, S. Yamada, Y. Yokoyama, Y. Kurita, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1677–1682; b) Y. Yokoyama, T. Tanaka, T. Yamane, Y. Kurita, *Chem. Lett.* **1991**, 1125–1128.

Received: February 20, 2011
Published Online: June 29, 2011

