DOI: 10.1002/ejoc.201001649

Photochromism of Rotation-Hindered Furylfulgides Influenced by Steric Modifications

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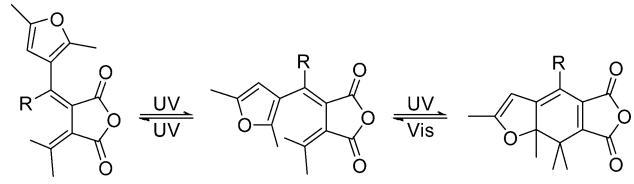
Keywords: Aldol reactions / Atropisomerism / Conformation analysis / Photochemistry / Photochromism

The syntheses of a bicyclic furylfulgide **14** and a (benzofuryl)-fulgide **15** with increased steric constraints are described. Their photochromic behaviors were analyzed by means of UV/Vis spectroscopic measurements, X-ray crystallography, and NMR experiments, and the results were compared to those of the furyl(methyl)fulgide **12** and the furyl(isopropyl)-fulgide **13**. Compounds **13E** and **14E** exhibit large quantum yields of 0.57 and 0.53 for the coloration reaction (*E*) → (*C*) compared with **12E** and **15E** (0.23 and 0.17). After irradiation with 350 nm light, **13E** and **14E** are transformed into the closed (*C*) forms almost quantitatively, whereas **12E** and **15E** result in a photostationary state with mixtures of the (*E*), (*Z*), and (*C*) forms. The crystal structures obtained for **13E**, **14E**, and **15E** show that the fulgides adopt cyclizable helical (*P*)-E_α conformations with no significant differences in atomic distances in the hexatriene unit. 2D- and temperature-dependent NMR experiments showed that the enantio- and diastereotopomerization processes were suppressed in a fulgide for the first time. Compound **14E** populates only the E_α conformational state. In contrast, **13E** and **15E** both exist in the cyclizable E_α and the non-cyclizable E_β conformations in solution. Due to the annulated benzene ring, **15E** exhibits a higher thermodynamic barrier than **13E**, so the "belly roll" process was reduced for **15**, but the (*E*) → (*Z*) isomerization could not be suppressed. The structural modification of **14** successfully suppressed the (*E*) → (*Z*) isomerization as well as the belly roll process. The way in which the isomerization reaction is suppressed by steric hindrance could not be fully elucidated by using these methods.

Introduction

Fulgides[1] are an important class of photoswitches that complement diarylethenes[2] and spiropyrans.[3] Upon wavelength-specific illumination, they undergo reversible color changes and are thus of great interest for a range of applications.[4] The first fulgides were synthesized by Stobbe in the early 20th century.[5] Like diarylethenes, they contain a hexatriene system with at least one phenylic or heterocyclic part as the central photochromic unit for the electrocyclic reaction. There are three different forms of fulgides, two mainly colorless, open forms, (*E*) and (*Z*), and a colored, closed form, (*C*). The photochromic behavior is depicted in Scheme 1. The photochromism can be monitored by UV/Vis spectroscopic methods, because there is a considerable change in the absorption spectra. Varyation of the substituents at the photochromic center causes a remarkable change in the electronic state of the fulgides and therefore affects the absorption spectra of the compounds. Electron-withdrawing groups lead to a bathochromic shift of the absorption maximum, whereas electron-donating substituents cause a hypsochromic shift.[6] Furthermore, heterocyclic moieties have a large influence on the spectroscopic quality. The open form of furylfulgides exhibits an absorption maximum at about 340 nm, whereas electron-rich indolylfulgides show a remarkable bathochromically shifted absorption maximum at about 400 nm.[7]



Scheme 1. Photochromic reaction of furylfulgides with variable substituents R at the photochromic core unit.

The fulgides of the first generation described by Stobbe had limited thermal stability, and the photochromic mechanism was intensively investigated only in the 1970s to 1980s.[8] A milestone in the history of fulgides was achieved by Heller and co-workers in 1981 with the development of a

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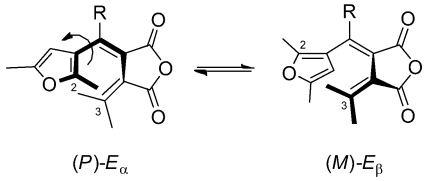
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201001649.

thermally stable fulgide.[9] The replacement of the hydrogen atoms at the cyclohexatriene unit by methyl groups and the introduction of a heterocyclic furyl moiety afforded fulgides that are stable towards both oxidation and hydrogen transfer. This formed the basis for current applications of fulgides, where high thermal and photochemical stability are essential.

Nevertheless, the efficiency of the photochromic reaction is limited by the photoisomerization of the open forms. The photochemical equilibrium between the (*E*) and the (*Z*) form is an unfavorable process that competes with the desired ring-closing reaction from the (*E*) to the (*C*) form. Therefore, the quantum yields for the coloration reaction are low, which is a significant disadvantage for potential applications. New results derived from femtosecond time-resolved measurements and DFT calculations show that, besides the (*E*) → (*Z*) isomerization, there are other deactivation processes that reduce the quantum efficiency.[10] In addition to the mentioned electronic substituent effects, steric modifications have great influence on the photochromism.[11] In 1988, Yokoyama et al. investigated the effects of bulky substituents R at the cylohexatriene moiety on the photochromic reaction of a furylfulgide.[12] The results showed that the quantum yield for (*E*) → (*Z*) isomerization becomes smaller, and the quantum yield for the (*E*) → (*C*) coloration process increases with the bulkiness of the substituents. In the case of an isopropyl substituent, no (*E*) → (*Z*) isomerization was observed, and a quantum yield for the coloration reaction of 0.58 was found. In comparison, the (*E*) → (*C*) quantum yield of the methyl compound **12** was determined to be only 0.19. Later, the influence of a *tert*-butyl substituent was described, which led to a quantum yield for the coloration process of 0.79.[13] For this reason, sterically hindered fulgides should be even more viable photochromic compounds for high-quality applications. Furthermore, Yokoyama indicated that, in addition to (*E*) → (*Z*) isomerization, the open (*E*) forms of furylfulgides undergo a diastereotopomerization of the helical structure between the (*P*)-E_α and (*M*)-E_β conformations.[14] The conversion between these two states occurs by a rotation of the furyl subunit, which Yokoyama called a "belly roll" process (Scheme 2).

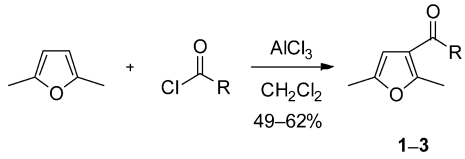


Scheme 2. Possible rotameric isomers of a furylfulgide. Due to the geometric constitution, (*M*)-E_β cannot undergo cyclization, whereas (*P*)-E_α is the cyclizable isomer.

It is clear that only molecules in the E_α conformation, wherein C-2 faces C-3, are in the correct geometric form to undergo the cyclization to the closed (*C*) isomer. If the rotation can be suppressed by structural manipulation of the fulgide backbone, all molecules will be available in the cyclizable E_α conformation, and the enantiotopomerization [(*P*)-E_α → (*M*)-E_α] and diastereotopomerization (E_α → E_β) processes would be blocked. Furthermore, the steric hindrance caused by the modification would be large enough to avoid the (*E*) → (*Z*) double bond isomerization. Herein, we report the synthesis of new furylfulgides that implement this concept. In (benzofuryl)fulgide **15** the formal benzo annulation of the furyl unit should limit its rotation to a minimal degree. To entirely eliminate the belly roll, a fulgide with a bicyclic framework **14** was designed and synthesized. Here, the rotation of the furyl ring is restrained by an alkyl chain connection between C-10 of the furyl moiety and C-6 of the hexatriene unit.

Results and Discussion

The furylfulgides **12**–**14** were synthesized by starting from commercially available 2,5-dimethylfuran and the appropriate acyl chloride (Scheme 3). The acylated compounds were obtained from a Friedel–Crafts reaction with $AlCl_3$ as catalyst. To minimize side reactions, the acylation was carried out at 0 °C under argon. Although it is known that furans polymerize in the presence of Lewis acids, the reactions gave moderate yields (49–62%).[15]

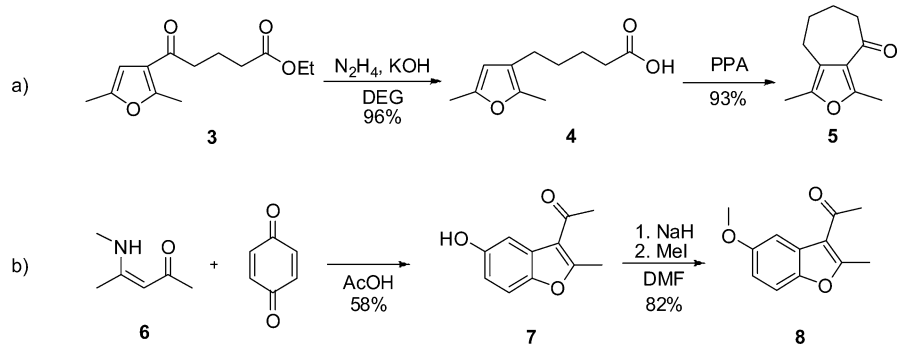


Scheme 3. Friedel–Crafts acylation of 2,5-dimethylfuran {**1** (R = Me), **2** (R = *i*Pr), **3** [R = $(CH_2)_3CO_2Et$]}.

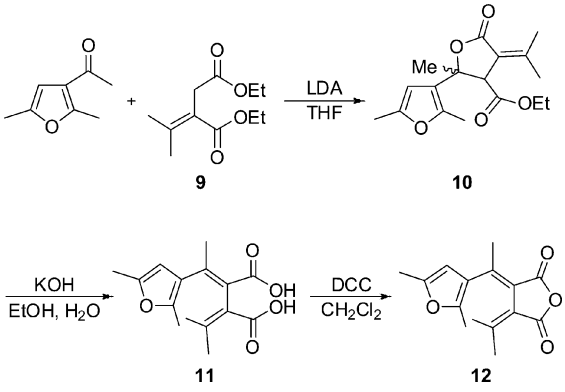
For the synthesis of the bicyclic furan **5**, the intermediate **3** was reduced in a Wolff–Kishner reduction under conditions described by Huang–Minlon in diethylene glycol (Scheme 4). After formation of a hydrazone with hydrazine, nitrogen was released by the action of potassium hydroxide at 200 °C. Simultaneously, the ester was saponified to the carboxylic acid[16] **4**, which decomposed slowly at room temperature, but was stable under argon at –20 °C. The cyclization process was catalyzed by polyphosphoric acid to give **5**. The Benzofuran compound **7** was synthesized in a Nenitzescu-type reaction by starting from *p*-benzoquinone and enamine ketone **6**. The reaction was carried out in glacial acetic acid, and the pure product precipitated from the solution after a few minutes at room temperature.[17] The hydroxy group was protected by methylation with methyl iodide to give **8**.

The limiting step in the fulgide synthesis is the Stobbe condensation between the heterocyclic ketones **1**, **2**, **5**, and **8**, and the diethyl isopropylidenesuccinate **9**.[18] Scheme 5 shows the synthesis of **12** as an example.

Treatment of **9** with lithium diisopropylamide (LDA) at –78 °C and addition of the heterocyclic compound gave a mixture of isomeric lactones **10**. These intermediate prod-



Scheme 4. (a) Synthesis of bicyclic ketone **5** by reduction and cyclization (DEG = diethylene glycol; PPA = polyphosphoric acid). (b) Nenitzescu-type reaction to form benzofuran **7** and subsequent methylation to give **8**.

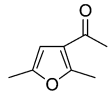
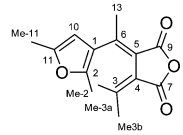
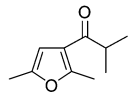
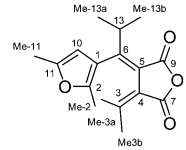
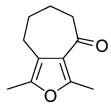
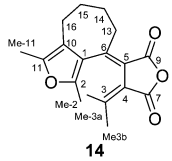
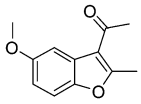
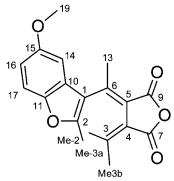


Scheme 5. Synthesis of **12** by Stobbe condensation. Saponification of lactone mixture **10** gave diacid **11** as a mixture of (*E*)/(*Z*) isomers, followed by dehydration to give a mixture of **12E** and **12Z**.

ucts were only detected by analytical methods (TLC, GC–MS, and ^{1}H NMR spectroscopy). After aqueous workup, the reaction mixture was filtered through silica gel. The crude product was dissolved in ethanol and treated with saturated aqueous KOH solution at 70 °C to give the diacid **11** as a mixture of (*E*)/(*Z*) isomers. For anhydride formation, the crude diacid was dissolved in dichloromethane, and *N*,*N*′-dicyclohexylcarbodiimide (DCC) was added. After stirring for 24 h at room temperature, the fulgides were obtained as a mixture of (*E*) and (*Z*) isomers. The isomers were separated by column chromatography with different mixtures of cyclohexane and ethyl acetate as eluent. A slight excess of the (*E*) isomer over the (*Z*) isomer was obtained (ratio of 1.2–1.5:1). The two isomers of **12**–**15** can easily be distinguished by their ^{1}H NMR spectra. Whereas the (*E*) forms show an intense methyl group signal arising from the isopropylidene group (CH_3-3a; $\delta \approx 1.3$ ppm) in $CDCl_3$, the corresponding signal of the (*Z*) isomer is shifted downfield ($\delta = 2.1$–2.3 ppm). Furthermore, all (*Z*) forms exhibit lower R_f values than the corresponding (*E*) isomers by approximately 10%.

Fulgides **12**–**15** exhibit the expected photochromic behavior of furylfulgides. The absorption maxima (λ_{max}) of the open (*E*) isomers show a strong absorption band at about 330–350 nm in the near-UV region. The λ_{max} values of the (*Z*) isomers are shifted by around 20 nm to longer wavelengths. The closed (*C*) isomers have an absorption maximum near 470–490 nm (Table 1).

Table 1. List of the synthesized fulgides **12**–**15** and precursors, together with their UV/Vis spectroscopic data {λ_{max} [nm], (ε_{max} [L mol^{-1} cm^{-1}])}.

Ketone	Fulgide[a]	E[b]	Z[b]	C[b]
 1	 12	336 (6615)	350 (8906)	472 (9328)
 2	 13	336 (4125)	352 (4560)	476 (9038)
 5	 14	344 (4715)	364 (8145)	491 (9560)
 8	 15	329 (6790)	345 (8680)	485 (9623)

[a] The atom numbering of each fulgide is arbitrary. [b] 10^{-4} M solution in *n*-hexane at room temp.

Figure 1 shows the evolution of the absorption spectrum of **14E** upon successive irradiation with 350 nm light. The absorption band near 350 nm decreases to a minimal amount, while the strong band near 500 nm belonging to the (*C*) isomer increases. Irradiation with 500 nm light leads back to the initial spectrum of the (*E*) isomer. A similar behavior can be observed for **13E**. However, solutions of

12E and **15E** exhibit different characteristics upon irradiation with 350 nm light. The (*C*)/(*Z*)/(*E*) ratios in the photostationary states were analyzed by NMR spectroscopy. A solution of each (*E*) isomer in $CDCl_3$ was successively irradiated with 350 nm light. The results show that, for **13** and **14**, after an irradiation time of 90 min, the fulgides were almost quantitatively transformed into the closed (*C*) forms. As for **13E**, the (*E*) → (*Z*) isomerization is suppressed in **14E** due to the steric hindrance at C-6. In the cases of **12** and **15**, an equilibrium is established between all three isomers in the photostationary states after an irradiation time of 90 min. For **12**, the conformation ratio (*C*)/(*Z*)/(*E*) is 1:0.15:0.15, and for **15** the ratio is 1:0.65:0.83. These results show that the structural modification in **15** does not suppress the (*E*) → (*Z*) isomerization. An explanation for these different photochemical properties caused by steric or electronic differences can be derived from femtosecond time-resolved transient absorption spectroscopy.[10] In particular, the time-resolved measurements revealed that the photo-induced ring-closure reactions are considerably faster in the cases of **13** and **14** ($\tau \approx 50$ fs) compared with **12** and **15** ($\tau \approx 110$ and 140 fs, respectively). Thus, the molecule-specific dynamics in the excited electronic states appear to play decisive roles.

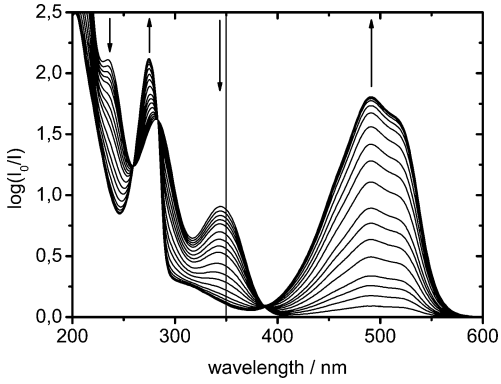


Figure 1. Irradiation of **14E** with 350 nm light ($I = 1.10 \times 10^{-6}$ mol·s^{-1}·L^{-1}; time: 0, 0.25, 0.5, 0.75, 1, 1.5, 2, 2.5, 3, 4, 5, 6, 7.5, 9.5, 11.5, 14.5, 18.5, 23.5, 28.5, 33.5 min).

The quantum yields for the photoisomerization reactions of fulgides **12**–**15** in *n*-hexane were determined by using the methods described by Uhlmann and Gauglitz[19] or Maafi[20] and are given in Table 2. For the known compounds **12** and **13**, the results are in good agreement with data reported in the literature. Some differences can be found for the value of ϕ_{CE} at 335/365 nm of **12**. However, a range from 0.00 (ϕ_{CE}) up to 0.12 (ϕ_{CE}) is given in the literature, which can be rationalized by the low absorption coefficients of the (*C*) forms at 365 nm.[19,21] In practice, only an irradiation wavelength around 500 nm appears to be suitable for the (*C*) → (*E*) isomerization and for the determination of ϕ_{CE}.

For fulgides **13E**, **14E**, and **15E**, X-ray crystallographic analyses gave structural information for the solid state (Table 3). All (*E*) isomers adopt the (*P*)-E_a conformation in a helical structure in the crystal, and the bond lengths inside the hexatriene units of the fulgides show no significant differences. Compared to the distance between the two ring-closing atoms C(2) and C(3) of **12E** [0.3445(4) nm],[14a] only a small deviation is observed for **13E** [0.3426(2) nm], **14E** [0.3559(2) nm], and **15E** [0.3663(2) nm]. Therefore, the interatomic distances do not provide an explanation for the different photochemical properties. The dihedral angles C(9)–C(5)–C(4)–C(3) are also comparable [148.82(11)° for **13E**, 144.83(11)° for **14E**, and 146.29(13)° for **15E**]. Compound **14E** has a strained geometry due to the cycloheptyl ring, which leads to an extension of the dihedral angle C(5)–C(6)–C(1)–C(10) to 151.11(11)° compared with 138.14(10)° for **13E** and 136.83(13)° for **15E**. The complete crystallographic data for **14** and **15** will be published elsewhere.[22]

Table 2. Isomerization quantum yields of fulgides **12**–**15**.

Compound	ϕ_{EC}[a]	ϕ_{EZ}[a]	ϕ_{CE}[a]	ϕ_{ZE}[a]
12	$0.23_{(335)}$	$0.13_{(335)}$	$0.06_{(335)}$, $0.10_{(500)}$	$0.10_{(335)}$
13	$0.57_{(335)}$	0.00	$0.12_{(335)}$, $0.09_{(500)}$	–[b]
14	$0.53_{(350)}$	0.00	$0.13_{(350)}$, $0.07_{(500)}$	–[b]
15	$0.17_{(330)}$	$0.15_{(330)}$	$0.21_{(330)}$, $0.16_{(500)}$	$0.11_{(330)}$

[a] Irradiation wavelengths [nm] are given as subscripts in parentheses. [b] Not determined.

Table 3. Selected interatomic distances and dihedral angles of X-ray structures of **13E**, **14E**, and **15E**.

Compound	Distance [nm] C(2)–C(3)	Dihedral angle [°] C(9)–C(5)–C(4)–C(3)	Dihedral angle [°] C(5)–C(6)–C(1)–C(10)
13E	0.3426(2)	148.82(11)	138.14(10)
14E	0.3559(2)	144.83(11)	151.11(11)
15E[a]	0.3663(2)	146.29(13)	136.83(13)
	0.3540(2)	152.36(13)	129.36(13)

[a] Two molecules are present in the unit cell, one of which showing strained angles due to packing effects.

NMR experiments were carried out to assess the conformational properties of the furyl fulgides **13E**, **14E**, and **15E**. The assignments were made by comparison with previously assigned furyl fulgides[23] and on the basis of correlations in two-dimensional gCOSY, HSQC, and HMBC experiments. Specifically for **14E**, C-7 and C-9 were distinguished in the HMBC experiments by the presence of a ^4J coupling between H(Me-3a/b) and C-7, whereas C-4 and C-5 were established by strong ^3J correlations to H(Me-3a/b) and 16a/b-H, respectively. The former correlations also distinguished 13a/b-H from 16a/b-H, because the latter in turn shows correlations to to C-11 of the furyl ring. These correlations distinguish C-11 from C-2, allowing for the assignments of C(Me-11) and C(Me-2) from ^2J cross peaks. The ^3J cross peaks of H(Me-11) and H(Me-2) then unambiguously identify C-10 and C-1, respectively.

NMR experiments at variable temperatures were utilized to detect chemical-exchange processes such as rotational barriers in the fulgides. At room temperature, the spectrum of **14E** is characterized by one set of resonances for all methyl groups, indicating the presence of only one rotamer (or fast conversion between the conformers). The prochiral methylene ring protons in the cycloheptyl ring, however,

lead to sharp, well-separated resonances with clear coupling patterns that are very similar to those of the clearly distinguishable prochiral methyl groups in furyl(isopropyl)fulgide **13E**.

Thus, NMR spectra of **14E** were acquired at elevated temperatures up to 318 K and compared to those of **13E** (Figure 2). For **13E**, it had been shown that the methyl groups exchange frequencies at elevated temperatures, with a coalescence temperature of approximately 338 K (Figure 2b).[14b,23] In contrast, the spectra of **14E** were devoid of any line broadening, even at the highest achievable temperature, suggesting the absence of any racemization. This was confirmed by NOESY/EXSY experiments performed at 323 K, which were void of any negative exchange cross-peak contributions.

To detect additional rotation barriers, the temperature of the NMR probe was lowered from room temperature to 178 K. In the data for **13E**, subtle chemical-shift changes were observed throughout the fulgide spectra (Figure 3a). All resonance linewidths changed almost imperceptibly and uniformly, consistent with an increase due only to solvent-viscosity changes (and increasing difficulties in attaining a homogeneous magnetic field through shimming). No further barrier was detected. For **14E**, a kinetic barrier with a coalescence temperature of about 210 K (Figure 2c) was observed. Below this transition, two sets of signals are present in a ratio of 1:2.5. Most noticeable is the resonance doubling for 13a-H, with two resonances of similar multiplicities at δ = 4.20 and 3.82 ppm at 178 K. The signal of 16a-H also splits, but the upfield-shifted second resonance is superimposed by those of the methyl groups. For the methyl groups, the doubling is best seen for H(Me-3b) and H(Me-2) owing to the larger shift difference between the peaks.

Racemization of fulgides has been suggested to occur through a three-step process, because the (*P*)-$E_\alpha \rightarrow$ (*M*)-E_α enantiotopomerization/helical chirality inversion is prohibited by steric overlap.[14a] For **13E**, the belly-roll process ($E_\alpha \rightarrow E_\beta$) converts the helical chirality in concert with the rotation around the C-1–C-6 bond. The enantiotopomerization [(*P*)-$E_\beta \rightarrow$ (*M*)-E_β] has the higher barrier of 53 kJ mol^{-1} and is responsible for the coalescence observable at high temperature (Figure 2b).[14] The barrier for the equivalent process in **14E** can only be similar or higher, ow-

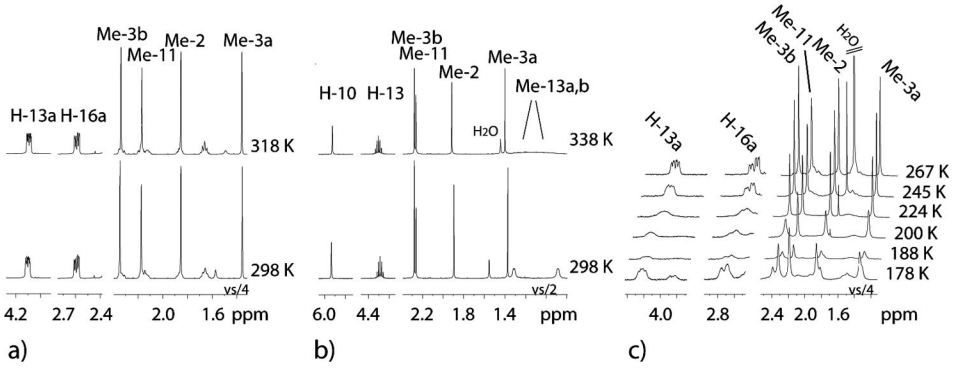


Figure 2. (a) 1D ^{1}H NMR spectra of **14E** at 298 and 318 K. Neither linewidth nor chemical shift change appreciably for any line, including the strongly diastereotopic 13a-H or 16a-H (at δ = 4.10 and 2.60 ppm, respectively). (b) 1D ^{1}H NMR spectra of **13E** at elevated temperatures from 298 to 338 K. (c) Expanded regions of the 1D ^{1}H NMR spectra of **14E** (200 MHz, CD_2Cl_2) at variable temperatures. The vertical scale of the 13a-H and 16a-H protons (left panel) is increased four-fold versus the upfield region (right panel).

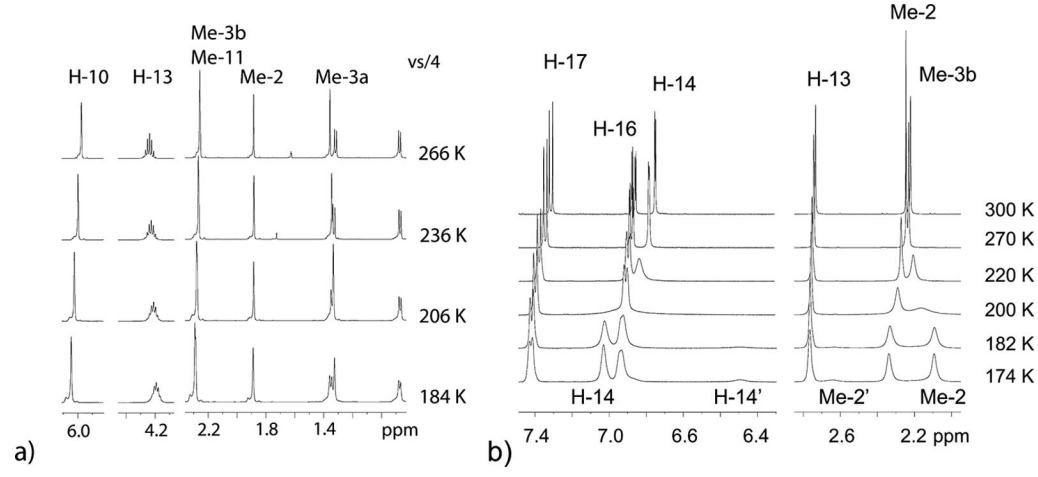


Figure 3. (a) Low-temperature 1D ^{1}H NMR spectra of **13E** (500 MHz, CD_2Cl_2). (b) 1D ^{1}H NMR spectra of **15E** at variable temperatures (200 MHz, CD_2Cl_2).

ing to larger steric hindrance in **14E**. Most importantly, the cyclic analogue **14E** does not show this coalescence, indicating that the $E_\beta \rightarrow E_\beta$ conversion was successfully prevented (the respective coalescence temperature raised beyond detection), thus indicating that a non-racemizing fulgide was synthesized.

Interestingly, a low-temperature transition was observed for **14E**, which, in principle, could originate either from the belly roll or from an alternative rotational barrier. Energy calculations of favorable ring conformations of **14E** suggest that the E_β conformation is 35 kJ/mol less stable then the E_α conformation. An interconversion between these rotamers would thus be expected to have a rotational barrier much higher than 35 kJ/mol, and thus lead to a chemical exchange process above room temperature. Furthermore, an energy difference of 35 kJ/mol results in a population fraction of 100% of the E_α conformer by using Boltzmann's distribution, whereas the ratio determined from NMR spectroscopic measurements was 1:2.5. It is far more likely instead that the low-temperature interconversion stems from two favorable, energetically nearly equal conformations of the cycloheptyl moiety (Figure 4). This agrees well with the observed chemical shift difference between the respective rotamer resonances, with the largest shift differences being observed for 13-H and 16-H, and with typical coalescence temperatures for ring inversion.[24] Furthermore, the signals of the isopropylidene methyl groups H(Me-3a/b) shift noticeably, because their location beneath the furyl ring makes them particularly sensitive to furyl ring rotation owing to the ring current effect.

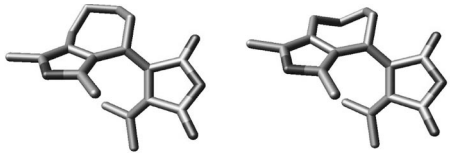


Figure 4. Calculated conformers of **14E**$_\alpha$. Ground-state geometry optimizations were performed at the DFT/B3LYP/6-31+G(d,p) level by using Gaussian 09.[25] The calculated energy difference is approx. 6 kJ/mol, which results in a population fraction of approximately 0.9 of the more stable conformer (right) at room temperature by using Boltzmann's distribution. The left conformer matches the experimental X-ray crystallographic structure (carbon atoms grey, oxygen atoms dark grey).[22]

Due to the absence of any diastereotopic groups in (benzofuryl)fulgide **15E**, the enantiotopomerization at high temperatures cannot be detected. As expected, the compound exhibits only one set of resonances at room temperature. At low temperatures, however, a rotational barrier is detectable (Figure 3b). In dichloromethane the NMR analysis at 500 MHz reveals that the coalescence is clearly observable for 14-H (ca. 200 K) in the benzylic ring and the furyl methyl group H(Me-2) (ca. 190 K), leading to an estimate for the rotational energy barrier of 37 kJ/mol. The corresponding proton chemical shifts for the two rotamers at low temperatures were established by a 2D-EXSY experiment. The ratio between rotamers is approximately 6:1, which is in excellent agreement with the calculated fraction of the E_α conformer of 82% and 18% of the E_β conformer.[10] Based on the knowledge of rotational barriers in the furylfulgide, it is likely that the $E_\alpha \rightarrow E_\beta$ conversion, which becomes visible in this furylfulgide analogue, is due to increased steric hindrance.

Conclusions

The synthesis of furylfulgides with different structural modifications, which greatly influence the isomerization processes of the photochromic compounds, has been developed. The modification at C-6/C-10 of the furyl backbone strongly affects the belly roll process, or even eliminates it completely. Whereas benzoannulation (**15**) reduced the belly roll process (*P*)-$E_\alpha \rightarrow$ (*M*)-E_β, and introduction of an isopropyl group (**13**) reduced the (*E*) $\rightarrow$ (*Z*) isomerization, both processes and enantiotopomerization were suppressed for the bicyclic furylfulgide **14**.

Experimental Section

General: All commercially available compounds, including 2,5-dimethylfuran and LDA (2 M in THF/*n*-heptane/ethylbenzene) were purchased from Acros, Alfa Aesar, or Sigma Aldrich and were used without further purification. Solvents were dried according to standard procedures. Column chromatography was performed with silica gel (0.040–0.063 mm, Macherey–Nagel). All NMR spectroscopic data were acquired with Bruker Avance 600, DRX 500, or Avance 200 spectrometers. 1D ^{1}H NMR, ^{13}C NMR, ^{13}C-cpd, DEPT135, gCOSY, HSQC, and HMBC were used for spectroscopic analysis. Samples were dissolved in $CDCl_3$, [D_6]DMSO, or in CD_2Cl_2 with TMS added as internal standard. Spectra were referenced to TMS or solvent lines [$CDCl_3$: δ = 7.24 ppm (^{1}H), 77.0 ppm (^{13}C); [D_6]DMSO: δ = 2.49 ppm (^{1}H), 39.5 ppm (^{13}C); CD_2Cl_2: δ = 5.30 ppm (^{1}H), 53.52 ppm (^{13}C)]. EI mass spectra were recorded with a VG Autospec X (Micromass Co. UK Ltd.) and HR mass spectra were performed with a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer APEX III (Bruker Daltonik GmbH, Bremen, Germany). The quantum yields of the photoisomerization reactions of fulgides **12**–**15** in *n*-hexane were determined by monitoring the evolution of the absorption spectra during irradiation of stirred solutions of the (*E*) isomers using a 150 W xenon lamp as light source and a monochromator for wavelength selection (typical spectral width $\Delta\lambda$ = 5–10 nm). All measurements were performed in a quartz cuvette with d = 1 cm pathlength for irradiation and absorption measurements. The irradiation intensities were determined with a power meter (Coherent, 3Σ, PS19Q), and the accuracy of the intensity measurements was checked by ferrioxalate actinometry.[26] Absorption spectra were measured with a Shimadzu UV-2401 desktop spectrometer.

General Preparation of 3-Acyl-2,5-dimethylfurans 1–3: The appropriate acyl chloride (47 mmol) was added to a suspension of $AlCl_3$ (6.67 g, 50 mmol) in dichloromethane (150 mL) under argon at 0 °C. After stirring for 1 h, 2,5-dimethylfuran (5.00 mL, 47 mmol) was added, and the solution immediately turned dark-red. After 30 min, the reaction mixture was cautiously hydrolyzed by addition of aqueous HCl (2 M), and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 100 mL), and 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 purified by column chromatography.

1-(2,5-Dimethylfuran-3-yl)ethanone (1): Yield: 53%; R_f = 0.36 (cyclohexane/ethyl acetate, 9:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.13 (s, 1 H, Ar-H), 2.47 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 194.2, 156.7, 149.8, 122.0, 106.0, 29.0, 14.2, 13.0 ppm. MS (70 eV): *m*/*z* (%) = 138 (55) [M^+], 123 (100) [M – CH_3^+], 81 (21), 43 (82).

1-(2,5-Dimethylfuran-3-yl)-2-methylpropan-1-one (2): Yield: 56%; R_f = 0.61 (cyclohexane/ethyl acetate, 9:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.16 (s, 1 H, Ar-H), 3.01 (sept, $^3J_{H,H}$ = 6.6 Hz, 1 H, CH), 2.52 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3), 1.11 (d, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 201.0, 157.5, 149.7, 120.5, 105.7, 38.1, 18.6, 14.3, 13.2 ppm. MS (70 eV): *m*/*z* (%) = 166 (18) [M^+], 123 (100), 43 (28).

Ethyl 5-(2,5-Dimethylfuran-3-yl)-5-oxopentanoate (3): Yield: 62%; R_f = 0.23 (cyclohexane/ethyl acetate, 7:3). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.14 (s, 1 H, Ar-H), 4.07 (q, $^3J_{H,H}$ = 6.9 Hz, 2 H, CH_2), 2.67 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2), 2.47 (s, 3 H, CH_3), 2.32 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2), 2.18 (s, 3 H, CH_3), 1.92 (m, 2 H, CH_2), 1.19 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 195.7, 173.2, 156.9, 149.8, 121.4, 105.5, 60.2, 39.9, 33.3, 19.1, 14.2, 14.1, 13.1 ppm. MS (70 eV): *m*/*z* (%) = 238 (19) [M^+], 193 (23) [M – $OC_2H_5^+$], 192 (23), 123 (100), 43 (38).

5-(2,5-Dimethylfuran-3-yl)pentanoic Acid (4): Ester **3** (5.80 g, 24 mmol), KOH (6.86 g, 122 mmol), and hydrazine (3.54 mL, 73 mmol, 98% aq. sol.) were dissolved in diethylene glycol (150 mL) and heated to reflux at 160 °C. After 1 h, the residual hydrazine and water were distilled off, and the reaction mixture was heated to 195 °C for 4 h. The reaction mixture was neutralized with aqueous HCl (2 M) and extracted with ethyl acetate (4 × 75 mL). The combined organic layers were washed with saturated aqueous NaCl solution, dried with $MgSO_4$, and the solvent was removed in vacuo. The product **4** (4.50 g, 23 mmol, 96%) was used without further purification, but can be purified by column chromatography. R_f = 0.59 (cyclohexane/ethyl acetate, 7:3). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 11.08 (br. s, 1 H, COOH), 5.74 (s, 1 H, Ar-H), 2.34 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 2.27 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, CH_2), 2.19 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 1.60–1.66 (m, 2 H, CH_2), 1.48–1.54 (m, 2 H, CH_2) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 180.2, 149.1, 145.1, 118.9, 107.2, 33.9, 29.7, 24.4, 24.2, 13.4, 11.3 ppm. MS (70 eV): *m*/*z* (%) = 196 (34) [M^+], 123 (12), 110 (37), 109 (100), 95 (18), 43 (82).

1,3-Dimethyl-5,6,7,8-tetrahydrocyclohepta[*c*]furan-4-one (5): Polyphosphoric acid (14 g) was warmed to 80 °C, and **4** (4.50 g, 23 mmol) was added. After stirring for 15 min, the reaction mixture was hydrolyzed with water (120 mL) and extracted with ethyl acetate (4 × 75 mL). The combined organic layers were washed with saturated aqueous NaCl solution, dried with $MgSO_4$, and the solvent was removed in vacuo. Purification by column chromatography (cyclohexane/ethyl acetate, 9:1) gave the product **5** (3.74 g, 21 mmol, 93%) as a slightly yellow liquid. R_f = 0.31 (cyclohexane/ethyl acetate, 9:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.55 (m, 2 H, CH_2), 2.51 (m, 2 H, CH_2), 2.39 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 1.71–1.79 (m, 4 H, CH_2) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 199.5, 155.8, 144.5, 122.5, 117.7, 42.3, 25.5, 22.4, 22.1, 13.6, 10.9 ppm. HRMS: *m*/*z* calcd. for $C_{11}H_{14}O_2$ [M^+] 178.09938; found 178.09900.

(*Z*)-4-Methylaminopent-3-en-2-one (6): Methylamine (10 mL, 0.12 mol, 40% aq. sol.) was added to acetylacetone (10.30 mL, 0.10 mol) and stirred at room temperature for 2 h. After the exothermic reaction had 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 with saturated aqueous NaCl solution, and dried with $MgSO_4$. All volatile compounds were removed in vacuo, and the product was recrystallized from diethyl ether. Compound **6** was obtained as colorless needles (10.52 g, 0.09 mol, 90%), which sublimed in high vacuum. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): 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, $CDCl_3$, 25 °C): δ = 194.6, 164.0, 95.0, 29.3, 28.6, 18.5 ppm. MS (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 (7):[17] To a solution of *p*-benzoquinone (2.13 g, 20 mmol) in glacial acetic acid (80 mL), compound **6** (2.33 g, 21 mmol), dissolved in glacial acetic acid (30 mL), was added. In an exothermic reaction, a colorless precipitate formed after a few minutes. After stirring for 2 h, the precipitate was filtered off, washed with water and a small amount of diethyl ether, and dried in vacuo. The product **7** (2.19 g, 12 mmol, 58%) was used without further purification but can be recrystallized from glacial acetic acid. ^{1}H NMR (500 MHz, [D_6]-DMSO, 25 °C): δ = 9.31 (s, 1 H, OH), 7.35 (m, 2 H, Ar-H), 6.73 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 2.5 Hz, 1 H, Ar-H), 2.72 (s, 3 H, CH_3), 2.53 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, [D_6]DMSO, 25 °C): 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 (70 eV): *m*/*z* (%) = 190 (51) [M^+], 176 (11), 175 (100), 147 (13), 43 (20).

1-(5-Methoxy-2-methylbenzofuran-3-yl)ethanone (8): Compound **7** (1.20 g, 6 mmol) was dissolved in dimethylformamide (40 mL), and sodium hydride (0.30 g, 7 mmol, 60% susp.) was added at 0 °C under argon. After stirring for 1 h, methyl iodide (0.47 mL, 7 mmol) was added, and the reaction mixture was stirred at room temperature for an additional 2 h. The reaction was quenched by addition of aqueous HCl (50 mL, 2 M), and the aqueous layer was extracted with ethyl acetate (3 × 75 mL). The combined organic layers were washed with saturated aqueous NaCl solution, dried with $MgSO_4$, and the solvent was removed in vacuo. The product was purified by flash column chromatography (cyclohexane/ethyl acetate, 7:3) and recrystallization from cyclohexane. Compound **8** (1.00 g, 5 mmol, 82%) was obtained as yellow crystals. R_f = 0.64 (cyclohexane/ethyl acetate, 7:3). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.46 (d, $^4J_{H,H}$ = 2.5 Hz, 1 H, Ar-H), 7.31 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, Ar-H), 6.86 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 2.5 Hz, 1 H, Ar-H), 3.86 (s, 3 H, CH_3), 2.75 (s, 3 H, CH_3), 2.60 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): 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 (70 eV): *m*/*z* (%) = 205 (11), 204 (74) [M^+], 190 (17), 189.0 (100) [M – CH_3^+], 174 (9) [M – 2 CH_3^+], 161 (10), 147 (7), 118 (7), 90 (6), 82 (6), 63 (8).

Diethyl 2-Isopropylidenesuccinate (9):[27] Diethyl succinate (9.62 mL, 57.40 mmol) was added to a solution of potassium *tert*-butoxide (6.78 g, 0.06 mmol) in *tert*-butyl alcohol (75 mL). After stirring for 1 h, acetone (4.20 mL, 57.40 mmol) was added, and the reaction mixture was heated to reflux for 20 h. The reaction mixture was acidified with aqueous HCl (2 M) and extracted with diethyl ether (4 × 70 mL). The combined organic layers were washed with saturated aqueous NaCl solution, dried with $MgSO_4$, and all volatile compounds were removed in vacuo. The dark residue was dissolved in ethanol (140 mL) and acidified with concd. HCl (7 mL). After stirring at room temperature for 48 h, the reaction

mixture was neutralized with saturated aqueous $NaHCO_3$ solution and extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with water, saturated aqueous NaCl solution, dried with $MgSO_4$, and all volatile compounds were removed in vacuo. Distillation at 0.07 mbar gave **9** as a colorless liquid (2.63 g, 8.94 mmol, 60%). B.p. 67–70 °C (0.07 mbar). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 4.09 (q, $^3J_{H,H}$ = 6.91 Hz, 2 H, CH_2), 4.05 (q, $^3J_{H,H}$ = 6.91 Hz, 2 H, CH_2), 3.28 (s, 2 H, CH_2), 2.06 (s, 3 H, CH_3), 1.78 (s, 3 H, CH_3), 1.19 (t, $^3J_{H,H}$ = 6.91 Hz, 3 H, CH_3), 1.16 (t, $^3J_{H,H}$ = 6.91 Hz, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 171.3, 167.7, 148.7, 120.6, 60.5, 60.1, 35.3, 23.1, 23.1 ppm. MS (70 eV): *m*/*z* (%) = 214 (2) [M^+], 169 (55), 168 (76), 141 (14), 140 (28), 113 (23), 112 (100), 96 (13), 95 (52), 68 (19), 67 (58), 59 (14), 53 (16).

General Preparation of Fulgides 12–15:[18] A solution of **9** (15 mmol) in THF (15 mL) was cooled to –78 °C, and LDA (7.5 mL, 15 mmol, 2 M in 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 by using a syringe. The reaction mixture was warmed to room temperature overnight and stirred for an additional 24 h. The progress of the reaction was monitored by TLC. Upon completion, 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 removed in vacuo. The residue was dissolved in ethanol (60 mL), and a saturated aqueous solution of KOH (5 mL) was added. After stirring at 70 °C for 20 h, 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 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 and recrystallization from appropriate solvents.

Fulgide 12E:[9] Yield: 8%; R_f = 0.31 (cyclohexane/ethyl acetate, 9:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 5.90 (s, 3 H, Ar-H), 2.55 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3), 1.97 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 163.8, 163.3, 153.7, 151.3, 148.3, 146.8, 124.2, 120.9, 119.1, 105.8, 26.8, 22.6, 22.2, 13.9, 13.3 ppm. MS (70 eV): *m*/*z* (%) = 260 (49) [M^+], 246 (16), 245 (100) [M – CH_3^+], 217 (21), 201 (17), 173 (24), 145 (16), 128 (14), 115 (12), 91 (12), 77 (12), 43 (66). HRMS: *m*/*z* calcd. for $C_{15}H_{16}O_4$ [M^+] 260.10486; found 260.10260.

Fulgide 12Z:[9] Yield: 6%; R_f = 0.17 (cyclohexane/ethyl acetate, 9:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 5.96 (s, 1 H, Ar-H), 2.40 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 2.06 (s, 3 H, CH_3), 1.93 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 163.7, 160.9, 153.8, 153.1, 150.3, 145.6, 121.8, 120.1, 119.4, 105.6, 26.8, 25.3, 22.3, 13.7, 13.3 ppm. MS (70 eV): *m*/*z* (%) = 260 (45) [M^+], 246 (16), 245 (100) [M – CH_3^+], 217 (23), 201 (21), 199 (16), 173 (29), 145 (19), 129 (15), 128 (17), 115 (15), 91 (14), 77 (15), 43 (79). HRMS: *m*/*z* calcd. for $C_{15}H_{16}O_4$ [M^+] 260.10486; found 260.10310.

Fulgide 13E:[21] Yield: 7%; R_f = 0.45 (cyclohexane/ethyl acetate, 7:3). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 5.01 (s, 1 H, 10-H), 4.26 (sept, $^3J_{H,H}$ = 6.9 Hz, 1 H, 13-H), 2.23 (s, 3 H, Me-11), 2.25 (s, 3 H, Me-3b), 1.87 (s, 3 H, Me-2), 1.34 (s, 3 H, Me-3a), 1.28 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, Me-13a), 0.85 [d, $^3J_{H,H}$ = 6.9 Hz, 3 H, Me-13b] ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 163.2 (s, C-9), 163.1 (s, C-7), 157.9 (s, C-6), 154.1 (s, C-3), 150.6 (s, C-11), 147.0 (s, C-2), 120.7 (s, C-4), 120.1 (s, C-5), 119.2 (s, C-1), 105.6 (d, C-10), 30.8 (d, C-13), 27.1 (q, Me-3a), 22.6 (q, Me-13b), 22.6 (q, Me-3b), 20.5 (q, Me-13a), 13.3 (q, Me-11), 12.8 (q, Me-2) ppm. MS (70 eV): *m*/*z* (%) = 289 (15), 288 (74) [M^+], 274 (14), 273 (74) [M – CH_3^+], 245 (41), 217 (15), 201 (27), 199 (26), 173 (17), 128 (16), 115 (17), 96 (23), 91 (17), 77 (15), 43 (100). HRMS: *m*/*z* calcd. for $C_{17}H_{20}O_4$ [M^+] 288.13616; found 288.13440.

Fulgide 13Z:[21] Yield: 5%; R_f = 0.32 (cyclohexane/ethyl acetate, 7:3). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 5.86 (s, 1 H, Ar-H), 2.81 (sept, $^3J_{H,H}$ = 6.9 Hz, 1 H, CH), 2.38 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 2.12 (s, 3 H, CH_3), 2.03 (s, 3 H, CH_3), 1.16 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 0.97 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 163.4, 161.3, 155.7, 153.3, 151.8, 149.8, 121.1, 120.0, 115.2, 106.3, 34.2, 26.6, 22.1, 21.8, 19.1, 13.4, 12.6 ppm. MS (70 eV): *m*/*z* (%) = 289 (15), 288 (78) [M^+], 273 (76) [M – CH_3^+], 245 (44), 227 (39), 217 (19), 201 (31), 199 (26), 173 (20), 128 (15), 115 (17), 96 (23), 91 (16), 43 (100).

Fulgide 14E: Yield: 6%; R_f = 0.75 (cyclohexane/ethyl acetate, 7:3). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C, TMS): δ = 4.10 (ddd, $^3J_{H,H}$ = 13, $^3J_{H,H}$ = 6, $^2J_{H,H}$ = 3 Hz, 1 H, 13a-H), 2.60 (ddd, $^3J_{H,H}$ = 15, $^3J_{H,H}$ = 7, $^2J_{H,H}$ = 2 Hz, 1 H, 16a-H), 2.35 (m, 1 H, 16b-H), 2.32 (s, 3 H, Me-3b-H), 2.20–2.08 (m, 2 H, 13b-H, 14a-H), 2.16 (s, 3 H, Me-11-H), 1.91–1.82 (m, 1 H, 15a-H), 1.84 (s, 3 H, Me-2-H), 1.70–1.60 (m, 2 H, 15b-H, 14b-H), 1.35 (s, 3 H, Me-3a-H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2, 25 °C TMS): δ = 163.8 (s, C-9), 163.4 (s, C-7), 153.9 (s, C-3), 152.8 (s, C-6), 146.0 (s, C-11), 145.2 (s, C-2), 125.3 (s, C-1), 121.1 (s, C-4), 118.5 (s, C-5), 117.6 (s, C-10), 34.0 (t, C-13), 29.2 (t, C-14), 28.0 (t, C-15), 26.7 (q, C-Me-3a), 24.2 (t, C-16), 22.4 (t, C-Me-3b), 13.3 (q, C-Me-2), 11.0 (q, C-Me-11) ppm. MS (70 eV): *m*/*z* (%) = 301 (20), 300 (100) [M^+], 285 (14) [M – CH_3^+], 257 (30), 243 (14), 241 (21), 213 (18), 128 (13), 115 (13), 43 (84). HRMS: *m*/*z* calcd. for $C_{18}H_{20}O_4$ [M^+] 300.13616; found 300.13550.

Fulgide 14Z: Yield: 5%; R_f = 0.65 (cyclohexane/ethyl acetate, 7:3). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.55–2.62 (m, 2 H, CH_2), 2.38 (s, 3 H, CH_3), 2.24 (m, 1 H, CH_2), 2.18 (m, 1 H, CH_2), 2.16 (s, 3 H, CH_3), 2.13 (s, 3 H, CH_3), 2.04 (m, 1 H, CH_2), 1.94 (s, 3 H, CH_3), 1.90 (m, 1 H, CH_2), 1.41–1.55 (m, 2 H, CH_2) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 163.8, 161.1, 153.4, 152.2, 151.2, 145.0, 121.8, 121.3, 118.2, 117.8, 37.6, 29.8, 28.4, 26.5, 25.2, 22.1, 13.3, 11.2 ppm. MS (70 eV): *m*/*z* (%) = 301 (21), 300 (100) [M^+], 285 (17) [M – CH_3^+], 257 (35), 255 (16), 243 (16), 241 (23), 239 (18), 229 (15), 213 (25), 211 (18), 185 (16), 128 (16), 115 (16), 43 (92). HRMS: *m*/*z* calcd. for $C_{18}H_{20}O_4$ [M^+] 300.13616; found 300.13330.

Fulgide 15E: Yield: 7%; R_f = 0.26 (cyclohexane/ethyl acetate, 9:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.31 (d, $^3J_{H,H}$ = 9 Hz, 1 H, 17-H), 6.88 (dd, $^3J_{H,H}$ = 9.3 Hz, 1 H, 16-H), 6.73 (d, $^3J_{H,H}$ = 3 Hz, 1 H, 14-H), 3.82 (s, 3 H, 19-H), 2.75 (s, 3 H, 13-H), 2.25 (s, 6 H, Me-3b-H, Me-2-H), 1.15 (s, 3 H, Me-3a-H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz, 25 °C): δ = 163.6 (s, C-9), 163.0 (s, C-7), 156.2 (s, C-15), 155.5 (s, C-3), 153.5 (s, C-2), 148.8 (s, C-11), 145.0 (s, C-6), 126.5 (s, C-10), 121.5 (s, C-5), 120.8 (s, C-4), 119.6 (s, C-1), 112.9 (d, C-16), 111.6 (d, C-17), 102.8 (d, C-14), 55.9 (q, C-19), 26.7 (q, C-Me-3a), 22.7 (q, C-Me-3b), 22.0 (q, C-13), 14.0 (q, C-Me-2) ppm. MS (70 eV): *m*/*z* (%) = 327.2 (22), 326.2 (100) [M^+], 311.2 (43), 309.2 (12), 283.2 (20), 281.2 (12), 267.2 (41), 265.2 (15), 253.2 (13), 239.2 (17), 223.2 (11), 204.1 (11), 165.1 (11), 162.1 (21),

152.1 (12), 115.1 (13), 106.1 (12), 91.1 (12), 77.1 (10), 44.0 (12), 43.0 (16). HRMS: *m/z* calcd. for $C_{19}H_{18}O_5Na^+$ [M^+] 349.10464; found 349.10480; calcd. for $(C_{19}H_{18}O_5)_2Na^+$ 675.22026; found 675.22007.

Fulgide 15Z: Yield: 5%; R_f = 0.11 (cyclohexane/ethyl acetate, 9:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.31 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, Ar-H), 6.83 (m, 2 H, Ar-H), 3.80 (s, 3 H, CH_3), 2.46 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 2.04 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 163.2, 160.9, 157.2, 156.0, 154.3, 148.9, 143.8, 127.6, 122.8, 121.3, 114.9, 111.7, 111.6, 103.0, 66.0, 27.2, 24.0, 22.4, 13.6 ppm. MS (70 eV): *m/z* (%) = 327 (21), 326 (100) [M^+], 311 (37) [$M - CH_3^+$], 309 (11), 283 (18), 281 (10), 267 (67), 265 (12), 253 (12), 239 (20), 227 (15), 204 (10), 162 (19), 152 (10), 115 (10). HRMS: *m/z* calcd. for $C_{19}H_{18}O_5$ [M^+] 326.11542; found 326.11390.

Supporting Information (see footnote on the first page of this article): Detailed evaluation of the quantum yields and evolution of ^{1}H NMR spectra of **12**–**15** upon successive irradiation.

Acknowledgments

This work was supported by the Biophotonics Initiative of the German Ministry of Research and Education (BMBF) (grant 13N9234) (F. S., J. M.) and funded by the Deutsche Forschungsgemeinshaft (SFB 677, "Function by Switching" (R. S., F. R., and F. T.).

[1] a) Y. Yokoyama, *Chem. Rev.* **2000**, *100*, 1717–1739; b) Y. Yokoyama, in *Molecular Switches* (Ed. B. L. Feringa), Wiley-VCH, Weinheim, **2001**, pp. 107–121.
[2] M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716.
[3] G. Berkovic, V. Krongauz, V. Weiss, *Chem. Rev.* **2000**, *100*, 1741–1753.
[4] a) S. Kawata, Y. Kawata, *Chem. Rev.* **2000**, *100*, 1777–1788; 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) S. Malkmus, F. 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; d) A. S. Dvornikov, E. P. Walker, P. M. Rentzepis, *J. Phys. Chem. A* **2009**, *113*, 13633–13644; e) F. M. Raymo, M. Tomasulo, *Chem. Soc. Rev.* **2005**, *34*, 327–336; f) J. Cusido, E. Deniz, F. M. Raymo, *Eur. J. Org. Chem.* **2009**, 2031–2045.
[5] a) H. Stobbe, *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 3673–3682; b) H. Stobbe, *Justus Liebigs Ann. Chem.* **1911**, *380*, 1–129; c) H. Stobbe, *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 3372–3382.
[6] a) Y. Yokoyama, T. Tanaka, T. Yamane, Y. Kurita, *Chem. Lett.* **1991**, 1125–1128; b) Y. Yokoyama, T. Sagisaka, Y. Mizuno, Y. Yokoyama, *Chem. Lett.* **1996**, 587–588; c) A. P. Glaze, H. G. Heller, J. Whittal, *J. Chem. Soc. Perkin Trans. 2* **1992**, 591–594.
[7] a) A. Kaneko, A. Tomoda, M. Ishizuka, H. Suzuki, R. Matsushima, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3569–3573; b) W. Zhao, Y. Ming, Z. Zhu, M. Fan, *J. Photochem. Photobiol. A: Chem.* **1992**, *63*, 235–240; c) L. Yu, Y. Ming, W. Zhao, M. Fan, *J. Photochem. Photobiol. A: Chem.* **1992**, *68*, 309–317.
[8] a) O. Crescente, H. G. Heller, S. Oliver, *J. Chem. Soc. Perkin Trans. 1* **1979**, 150–153; b) H. G. Heller, S. Oliver, M. Shawe, *J. Chem. Soc. Perkin Trans. 1* **1979**, 154–157; c) H. G. Heller, S. Oliver, *J. Chem. Soc. Perkin Trans. 1* **1981**, 197–201; d) A. Santiago, R. S. Becker, *J. Am. Chem. Soc.* **1968**, *90*, 3654–3658; e) M. Kaftory, *Acta Crystallogr., Sect. C* **1984**, *40*, 1015–1019.
[9] P. J. Darcy, H. G. Heller, P. J. Strydom, J. Whittal, *J. Chem. Soc. Perkin Trans. 1* **1981**, 202–205.
[10] R. Siewertsen, F. Strübe, J. Mattay, F. Renth, F. Temps, *Phys. Chem. Chem. Phys.* **2011**, *13*, 3800–3808.
[11] a) A. P. Glaze, H. G. Heller, J. Whittall, *J. Chem. Soc. Perkin Trans. 2* **1992**, 591–594; b) Y. Yokoyama, T. Iwai, N. Kera, I. Hitomi, Y. Kurita, *Chem. Lett.* **1990**, 263–264.
[12] Y. Yokoyama, T. Goto, T. Inoue, M. Yokoyama, Y. Kurita, *Chem. Lett.* **1988**, 1049–1052.
[13] J. Kiji, T. Okano, H. Kitamura, Y. Yokoyama, S. Kubota, Y. Kurita, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 616–619.
[14] a) Y. Yokoyama, K. Ogawa, T. Iwai, K. Shimazaki, Y. Kajihara, T. Goto, Y. Yokoyama, Y. Kurita, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1605–1612; b) Y. Yokoyama, T. Iwai, Y. Yokoyama, Y. Kurita, *Chem. Lett.* **1994**, 225.
[15] T. Reichstein, *Helv. Chim. Acta* **1930**, *13*, 356.
[16] A. Thurkauf, X. Chen, S. Zhang, Y. Gao, A. Kieltyka, J. W. F. Wasley, R. Brodbeck, W. Greenlee, A. Ganguly, H. Zhao, *Bioorg. Med. Chem. Lett.* **2003**, *13*, 2921–2924.
[17] T. I. Mukhanova, L. M. Alekseeva, E. F. Kuleshova, Y. N. Sheinker, V. G. Granik, *Pharm. Chem. J.* **1993**, *27*, 136–142.
[18] a) C. J. Thomas, M. A. Wolak, R. R. Birge, W. J. Lees, *J. Org. Chem.* **2001**, *66*, 1914–1918; b) M. L. Bossi, J. B. Rodriguez, P. F. Aramendia, *J. Photochem. Photobiol. A: Chem.* **2006**, *179*, 35–41.
[19] E. Uhlmann, G. Gauglitz, *J. Photochem. Photobiol. A: Chem.* **1996**, *98*, 45–49.
[20] M. Maafi, R. G. Brown, *Photochem. Photobiol. Sci.* **2008**, *7*, 1360–1372.
[21] Y. Yokoyama, T. Inoue, M. Yokoyama, T. Goto, T. Iwai, N. Kera, I. Hitomi, Y. Kurita, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 3297–3303.
[22] F. Strübe, J. Mattay, B. Neumann, H. G. Stammler, *Acta Crystallogr., Sect. C* **2011**, *67*, o33–o36.
[23] R. Siewertsen, F. Renth, F. Temps, F. Sönnichsen, *Phys. Chem. Chem. Phys.* **2009**, *11*, 5952–5961.
[24] R. K. Harris, R. A. Spragg, *J. Chem. Soc. B* **1968**, *6*, 684–691.
[25] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, Revision A.02, Gaussian, Inc., Wallingford, CT, **2009**.
[26] C. G. Hatchard, C. A. Parker, *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518–536.
[27] C. G. Overberger, C. W. Roberts, *J. Am. Chem. Soc.* **1949**, *71*, 3618–3627.

Received: December 8, 2010
Published Online: February 23, 2011

