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Synthesis and Photochemical Investigations of Tetrasubstituted Alkenes as Molecular Switches—The Effect of Substituents

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Dedicated to Professor Gerhard Bringmann on the occasion of his 60th birthday

Abstract: Molecular switches based on helical tetrasubstituted alkenes, substituted with either electron-withdrawing (CF_3, F, CN; **2a–c**, **3a**,**c**) or -donating substituents (Me, OMe; **2d**,**e**), have been synthesized from acyclic precursors **4** and **5** in a domino carbopalladation/Stille reaction. This palladium-catalyzed process allowed the rapid assembly of two C–C bonds, two six-membered rings, and the tetrasubstituted double bond in a completely diastereoselective fashion. The electronic effects of the substituents on the overall switching process were investigated by alternating irradiation of two different wavelength regions. Although the substituents had only a small influence on the absorption maxima, drastic differences in the switching behavior were observed.

Keywords: alkenes · domino reactions · molecular switches · substituent effects · UV/Vis spectroscopy

Introduction

Within the last 30 years the field of materials science in chemistry has progressed steadily. In particular, molecular machines, logic elements, and switches are a burgeoning field of research.[1] Molecular switches can be used for data storage, which is particularly relevant when considering the aspect of miniaturization.[1c–f] With the bistability of two distinct states being the prerequisite for a molecular switch, different external stimuli, such as light, electron transport, complexation and chemical reactions, can be used to interconvert between the two states.[2] Thus, the success of digital optical data systems, in which the recording and read-out of information is carried out by using light, has led to a shift from classic electronic semiconductor elements to light-driven molecular switches in academia. Although rotaxanes and certain transition-metal complexes featuring ambidentate ligands may be triggered electrochemically by oxidation or reduction, light is the preferred trigger for inducing rapid switching between states.[3,4] One of the key aspects of these molecular devices is the possibility of controlling the molecular motion at the smallest possible level. This allows for a subtle and distinct modification and governing of these molecules' functionality and potential applications.[5] To attain this goal, both a short and modular assembly of these compounds is needed. One way to ensure this is by making use of domino reactions in the overall synthetic process.[6] This would not only facilitate a rapid increase in molecular complexity but would also allow the reduction of time, reagents, and waste.

The chiroptical switches developed by Feringa and coworkers (e.g., **1**) containing a helical tetrasubstituted alkene moiety are particularly promising because their stable states can be accessed by using circularly polarized light.[7] Moreover, due to an additional thermal isomerization following photoinduced *P*/*M* isomerization, unidirectional motors have been effectively realized.[8] Herein we describe our approach to the synthesis of tetrasubstituted alkenes **2** and **3** containing electron-donating and -accepting substituents. Based on our previous successful approach[9] to the synthesis of unsubstituted aromatic helical alkenes (**2f**, **3f**, R = H), the substituted switches **2** and **3** (R = CF_3, F, CN, Me, OMe) can be retrosynthetically traced back to the acyclic precursors **4** and **5**, which lead to the alkynes **8** and either oxygen- or methylene-bridged aldehydes **6** or **7**, respectively. The key step of the synthetic route is the diastereoselective domino carbopalladation/Stille reaction of **4** and **5**, respectively, in which the two six-membered rings and the tetrasubstituted double bond are formed in one process (Scheme 1).

Acyclic tetrasubstituted alkenes have also recently been prepared stereoselectively by transition-metal-mediated reactions in the research groups of Lautens, Florent, Shi, Yu, Murakami, Tsuji, and Nakamura.[10]

In addition to the investigation of the effect of substituents (R = CF_3, F, CN, Me, OMe) on the domino reaction, the shape of the absorption spectra of **2** and **3** and their

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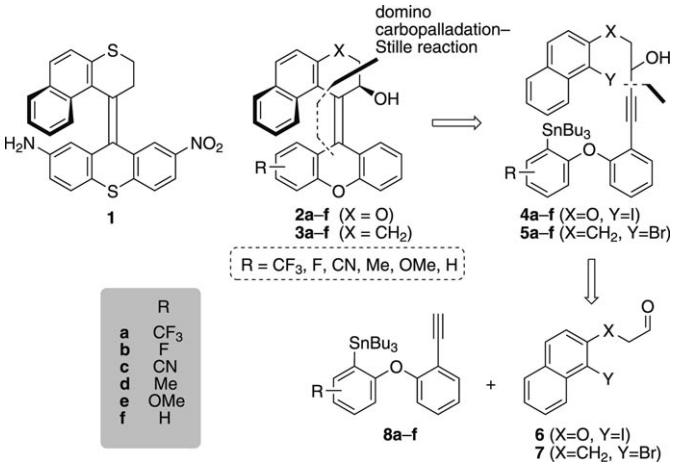
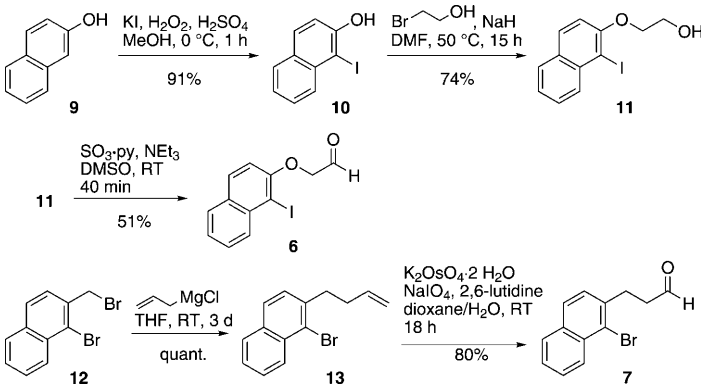


Scheme 1. Chiroptic molecular switches **1**–**3** and the retrosynthetic approach to their synthesis.

switching behavior under irradiation with light at two different wavelengths have also been examined.

Results and Discussion

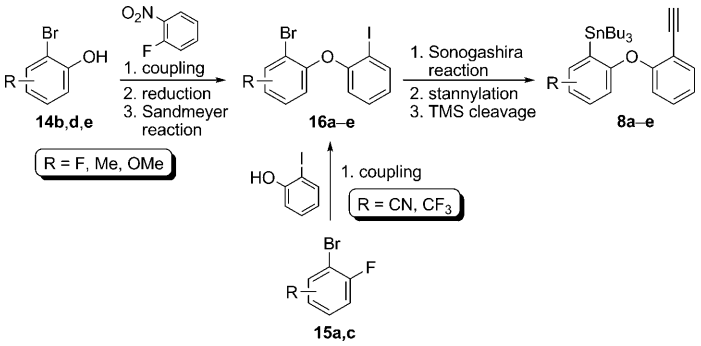
Synthesis of substituted alkenes 2a–e and 3a,c: For the synthesis of the substituted molecular switches **2** and **3**, we first synthesized the oxygen- or methylene-bridged aldehydes **6** and **7**, respectively, and the donor- and acceptor-substituted alkynes **8a–e**. The two fragments underwent coupling followed by a domino carbopalladation/Stille reaction. Aldehyde **6** was synthesized in three steps starting from 2-naphthol. The selective iodination was performed following a literature procedure[11] to give **10** in a yield of 91% (Scheme 2). After the reaction with 2-bromoethanol and NaH to afford **11** in a yield of 74%, the appended hydroxy group was oxidized by Parikh–Doering oxidation to afford the corresponding aldehyde **6** in a yield of 51%. The use of alternative oxidation reagents, for example, Dess–Martin periodinane or TPAP, did not lead to the desired product owing to the sensitivity of the iodide moiety. The methyl-



Scheme 2. Synthesis of the aldehydes **6** and **7**.

ene-bridged analogue **7** was accessed from commercially available substituted naphthalene **12**. Following the quantitative substitution reaction with freshly prepared allylmagnesium bromide the terminal double bond in **13** was oxidatively cleaved by using potassium osmate in the presence of 2,6-lutidine to give **7** in a yield of 80%.

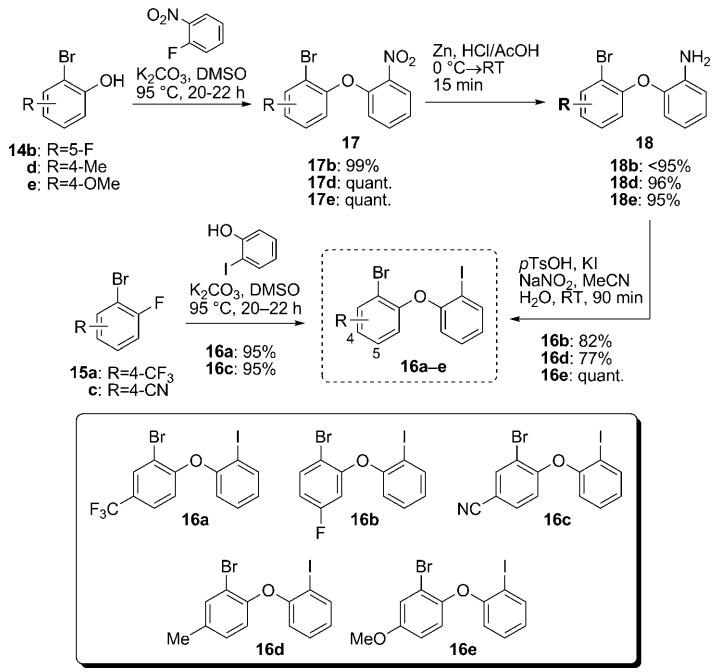
The substituted alkynes **8a–e** were synthesized according to the general reaction presented in Scheme 3. Depending on whether direct coupling of the different phenols **15** was



Scheme 3. General scheme for the synthesis of alkynes **8**.

possible either the direct reaction of **15** with 2-iodophenol or a three-step procedure starting from **14** and 2-fluoronitrobenzene was used. After the formation of **16**, the alkynes **8** were obtained by Sonogashira reaction with TMS-acetylene, stannylation, and subsequent removal of the TMS group. For the fluorine-substituted compounds, the three-step route to **16b** was chosen to avoid issues of regioselectivity in the primary coupling step.

The coupling of the fluoro- (**14b**), methyl- (**14d**), and methoxy-substituted (**14e**) phenols with 2-fluoronitrobenzene proceeded smoothly to give **17b**,**d**,**e** in almost quantitative yields. For the reduction of the nitro group in **17** zinc in strongly acidic media was used to afford the aromatic amines **18b**,**d**,**e** in yields of up to 96%. Under these conditions debromination of the substrates and products could be avoided. However, **18b** still contained small amounts (<5%) of the starting material **17b**, which could not be separated chromatographically. Therefore the mixture was used directly in the next step and gave the desired bromo-iodo-substituted ether **16b** in good yield (82%). The methyl- (**18d**) and methoxy-substituted (**18e**) amines were allowed to react under the modified Sandmeyer conditions developed by Krasnokutskaya et al.[12] and gave the desired diphenyl ethers in a yield of 77% (**16d**) and quantitatively (**16e**), respectively. By employing the same coupling conditions (K_2CO_3, DMSO, 95°C, 20–22 h) for the fluorobenzenes **15a** and **15c** bearing CF_3 and CN groups, respectively, the substituted ethers **16a** and **16c** were accessed in excellent yields (95% in both cases). Except for the fluorine-substituted derivative **16b**, which is substituted at C-5, all other compounds bear the donor/acceptor substituent at the *para* position with respect to the ether bridge (Scheme 4).

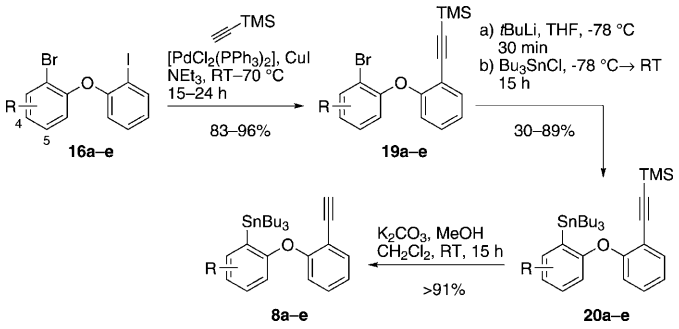


Scheme 4. Synthesis of diphenyl ethers **16a–e** and the substitution patterns for each system.

Following the synthesis of the aromatic ethers **16a–e**, the alkynes **8a–e** were obtained in three further steps. In the Sonogashira cross-coupling reaction, the acceptor-substituted arenes (**16a–c**) reacted smoothly at room temperature to give **19a–c** in high yields (83–96%). In contrast, the donor-substituted iodoarenes **16d** and **16e** reacted only sluggishly and elevated temperatures of 55–70°C were required to bring the reaction to completion, again with good yields of 88 and 94%, respectively. Apparently the inductive effect of the R group is sufficient to significantly influence the electronic properties of the right-hand aromatic ring, which results in a much reduced reactivity of the donor-substituted substrates. In the next step, the stannane residue was introduced by metal halide exchange with *t*BuLi[13] and subsequent reaction of the in situ formed organolithium compound with Bu_3SnCl. The stannanes **20a–e** were obtained in varying yields of 30–89%. The stannylation proved to be the critical step of the reaction sequence due to partial cleavage of the ether bridge. However, in the case of the cyano-substituted substrate **19c**, nucleophilic addition of *t*BuLi on the nitrile group led to a further reduction of the yield and gave the desired stannane **20c** in only 30%. The final TMS cleavage was affected by using methanol/CH_2Cl_2 in the presence of 50 mol% K_2CO_3. The desilylation was accomplished to give the desired alkynes **8a–e** in excellent yields of at least 91% in all cases (Table 1).

To prepare the substrates **4a–e** and **5a–e** for the domino reaction, the alkynes **8a–e** were coupled with the aldehydes **6** and **7**. The reaction was performed by deprotonating the alkynes **8** with LiHMDS as base followed by the very slow addition of the aldehyde in toluene through a syringe pump over 15 h. In this way, the propargylic alcohols could be obtained in average yields of 60–70%. In addition to the oxygen-bridged alcohols bearing an iodide, the corresponding bromides **22a–e** were also synthesized to investigate the effect of the halide on the ensuing domino carbopalladation/Stille reaction (Table 2).[14]

Table 1. Formation of alkynes **7a–e**.[a–c]

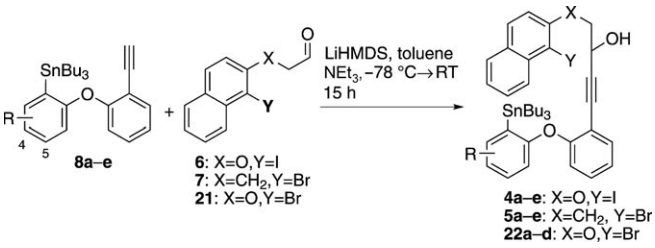


	R (substrate)	Yield Sonogashira reaction [%] (*T* [°C])[d]	Yield stannylation [%]	Yield TMS cleavage [%]
1	4-CF_3 (**16a**)	96 (RT)	89	91
2	5-F (**16b**)	83 (RT)	62	97
3	4-CN (**16c**)	83 (RT)	30	quant.
4	4-Me (**16d**)	88 (55)	49	97
5	4-OMe (**16e**)	94 (70)[e]	46	95

[a] Sonogashira coupling conditions: Substrate (1.0 equiv), TMS-acetylene (1.1 equiv), $[PdCl_2(PPh_3)_2]$ (0.02 equiv), CuI (0.04 equiv). [b] Stannylation conditions: Substrate (1.0 equiv), *t*BuLi (2.5 equiv), Bu_3SnCl (2.0 equiv). [c] TMS cleavage conditions: Substrate (1.0 equiv), K_2CO_3 (0.5 equiv). [d] Reaction temperature of the Sonogashira cross-coupling reaction. [e] NEt_3/DMF (1:1) was used as the solvent system.

With these compounds in hand, the domino reaction was studied. The desired alkenes **2a–e** and **3a**,**c** were obtained by using either the conditions for Stille reactions of Grasa and Nolan[15] ($Pd(OAc)_2$, IPr·HCl (**23**), TBAF, dioxane, 100°C, 38 h) or Fu and co-workers[16] ($[Pd_2dba_3]$, $PtBu_3$·HBF_4, CsF, dioxane, 80°C, 18 h). Neither the conditions recently developed by Naber and Buchwald using XPhos (**24**) nor the Herrmann–Beller palladacycle **25** led to the formation of the desired products in substantial amounts.[17,18] As expected, the iodo compounds **4a–d** generally gave higher yields than the corresponding bromo compounds **22a–d**. Subsequently all domino precursors were subjected to either the original[9] or the improved reaction conditions of Grasa and Nolan (Table 3). Apparently, the introduction of an acceptor moiety into **4** leads to an overall drop in the reactivity in the domino step because only the conditions introduced by Grasa and Nolan could effect the conversion to the desired alkenes **2a–c**. In contrast, the donor-substituted substrates **4d**,**e** gave the desired products **2d**,**e** by using either IPr or $PtBu_3$ as the ligand system. However, the latter methodology was superior with regards to the yields and purity of the products and henceforth was favored for electron-rich substrates. The formation of **3b**,**d**,**e** from **5b**,**d**,**e** was not possible using the conditions employed

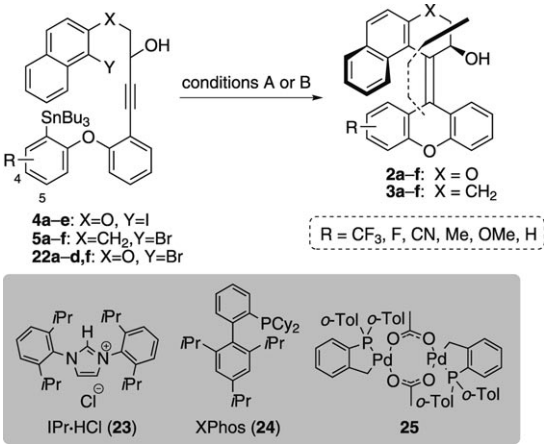
Table 2. Synthesis of propargylic alcohols **4a–e**, **5a–e**, and **22a–e**.[a]



Entry	R (substrate)	Aldehyde (X,Y)	Yield [%] (product)
1	4-CF_3 (**8a**)	**6** (O,I)	77 (**4a**)
2	4-CF_3 (**8a**)	**7** (CH_2,Br)	24 (**5a**)
3	4-CF_3 (**8a**)	**21** (O,Br)	66 (**22a**)
4	5-F (**8b**)	**6** (O,I)	61 (**4b**)
5	5-F (**8b**)	**7** (CH_2,Br)	77 (**5b**)
6	5-F (**8b**)	**21** (O,Br)	64 (**22b**)
7	4-CN (**8c**)	**6** (O,I)	82[b] (**4c**)
8	4-CN (**8c**)	**7** (CH_2,Br)	46[b] (**5c**)
9	4-CN (**8c**)	**21** (O,Br)	38[b,c] (**22c**)
10	4-Me (**8d**)	**6** (O,I)	65 (**4d**)
11	4-Me (**8d**)	**7** (CH_2,Br)	63 (**5d**)
12	4-Me (**8d**)	**21** (O,Br)	71 (**22d**)
13	4-OMe (**8e**)	**6** (O,I)	56 (**4e**)
14	4-OMe (**8e**)	**7** (CH_2,Br)	58 (**5e**)

[a] Reaction conditions: Alkyne (1.5 equiv), LiHMDS (1.5 equiv), NEt_3 (10 equiv), toluene, −78 °C→RT, 2 h; then at −78 °C: aldehyde (1.0 equiv) in toluene, 15 h. [b] The entire reaction was conducted at −78 °C. [c] Reaction conditions: Alkyne (1.0 equiv), LiHMDS (1.0 equiv), aldehyde (1.0 equiv), NEt_3 (10.0 equiv).

Table 3. Domino reactions of **4a–e**, **5a–f**, and **22a–d,f**.



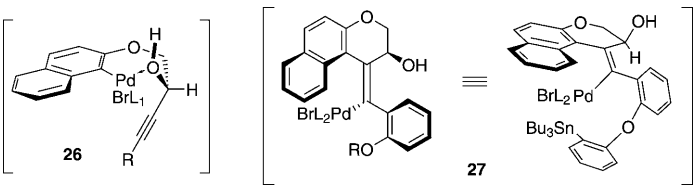
Entry	R (substrate)	X,Y	Conditions[a]	Yield [%] (product)
1	4-CF_3 (**4a**)	O,I	A	30 (**2a**)
2	4-CF_3 (**4a**)	O,I	B	traces (**2a**)
3	4-CF_3 (**22a**)	O,Br	A	10–20 (**2a**)[b]
4	4-CF_3 (**22a**)	O,Br	B	(**2a**)
5	4-CF_3 (**5a**)	CH_2,Br	A	29 (**3a**)[c]
6	5-F (**4b**)	O,I	A	33 (**2b**)[b][d]
7	5-F (**22b**)	O,Br	B	(**2b**)[e]
8	5-F (**5b**)	CH_2,Br	A	(**3b**)
9	4-CN (**4c**)	O,I	A	55 (**2c**)
10	4-CN (**22c**)	O,Br	A	24 (**2c**)
11	4-CN (**5c**)	CH_2,Br	A	19 (**3c**)[f]
12	4-Me (**4d**)	O,I	B	67 (**2d**)[c]
13	4-Me (**22d**)	O,Br	A	< 10 (**2d**)
14	4-Me (**22d**)	O,Br	B	< 10 (**2d**)[b]
15	4-Me (**5d**)	CH_2,Br	A	(**3d**)
16	4-OMe (**4e**)	O,I	A	traces (**2e**)
17	4-OMe (**4e**)	O,I	B	47 (**2e**)[b][c]
18	4-OMe (**5e**)	CH_2,Br	A	(**3e**)
19	H (**22f**)	O,Br	B	70 (**2f**)
20	H (**5f**)	CH_2,Br	B	55 (**3f**)

Abbreviations: dba: dibenzylideneacetone; TBAF: tetra-*n*-butylammonium fluoride. [a] Conditions A: $Pd(OAc)_2$, IPr·HCl (**23**), TBAF, dioxane, 100 °C, 36–38 h. Conditions B: [Pd_2dba_3], P*t*Bu_3·HBF_4, CsF, dioxane, 80 °C, 16–20 h. [b] Decomposition of the substrate. [c] The product was isolated as a 1:1 *E*/*Z* mixture. [d] The product was isolated as a 1:0.8 *E*/*Z* mixture. [e] Destannylation. [f] The product was isolated as a 10:1 *E*/*Z* mixture.

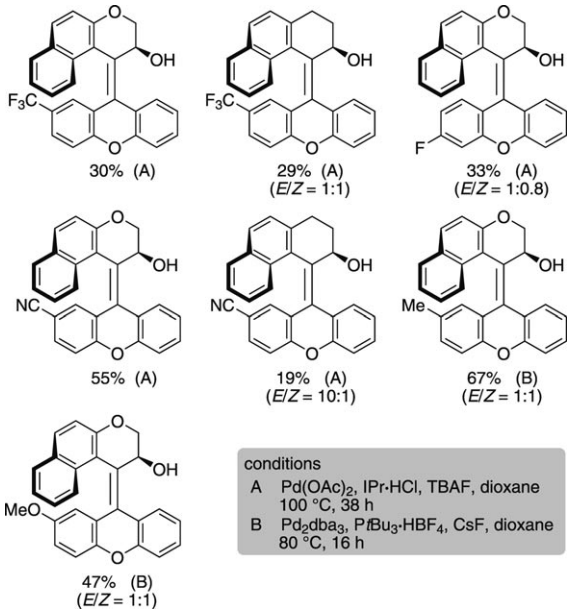
due to the decomposition of the starting materials. The rate-determining step of the entire sequence seems to be the oxidative addition reaction because neither the compounds stemming from only a carbopalladation or an intermolecular Stille reaction between two substrate molecules nor dehalogenated derivatives were detected as side-products. This was further underlined by the fact that when the corresponding bromine-derived substrates **22a–d** or **5a–e** were used, either decidedly lower yields or the decomposition of the substrates was observed, regardless of the conditions employed. Destannylation was observed in only one case (entry 8). The reactions of the unsubstituted bromo compounds **5f** and **22f**, which were synthesized in a prior study, are also included.

The reason for the observed differences in reactivity in the palladium-catalyzed domino step is not entirely clear. The steric hindrance of the substituents seems to be small and can probably be excluded. Because, as already mentioned, the oxidative addition reaction seems to be the rate-determining step one has to assume that the reason for the differences should be electronic in nature. A direct electronic influence through hyperconjugation can probably be precluded. However, a π–π interaction between the naphthalene moiety and the donor/acceptor-substituted phenyl rings might account for the observed differences in reactivity.

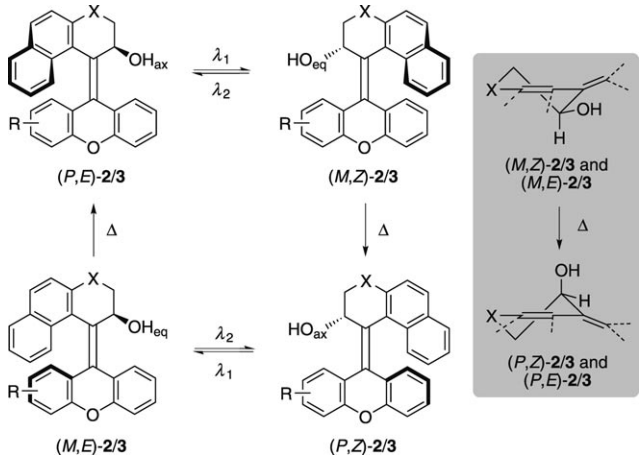
Earlier studies of the stereoselectivity of the domino reactions of **2f** and **3f** showed them to be completely diastereoselective.[9] The induced diastereoselectivity can be explained by an interaction between the palladium atom and the hydroxy group in the primarily assembled palladium intermediate **26**, which forces the alkyne moiety to lie below the naphthalene skeleton and thus controls the selective insertion into the triple bond via intermediate **27** (Scheme 5). In contrast, several of the newly synthesized compounds, which are depicted in Scheme 6, were obtained not in a dia-



Scheme 5. Proposed intermediates to explain the stereoselectivity in the domino carbopalladation/Stille reaction.



Scheme 6. Overview of the synthesized tetrasubstituted alkenes, reaction conditions, and diastereomeric ratios. Compounds **2f** and **3f** are taken from reference [9].



Scheme 7. Stepwise mechanism for the light-induced unidirectional switching process. Depiction of the half-chair conformers of the *M*,*Z* and *P*,*Z* forms showing the 1,3-allylic strain in (*M*,*Z*)-**2/3** and (*M*,*E*)-**2/3**.

stereomerically pure form but rather as a mixture of *E* and *Z* stereoisomers. However, this seems not to be due to a loss of selectivity in the domino reaction but rather due to the ability of these compounds to undergo a fast *E*/*Z* isomerization even in daylight.

Summarizing the synthetic work, the synthesis of **2a–f** and **3a**,**c**,**f** could be accomplished in six (**2a**,**c** and **3a**,**c**) or eight steps (**2b**,**d–f** and **3f**). In all cases the final step is the domino carbopalladation/Stille reaction, which yields the desired tetrasubstituted alkenes through the formation of two C–C bonds, two six-membered rings, and a tetrasubstituted double bond in a completely diastereoselective fashion. The procedure is highly flexible with regard to the substituents and allows rapid access to the desired alkenes with different substituents at different positions to allow structure–activity studies.

Photochemical investigation: The irradiation of (*P*,*E*)-**2/3** leads to a fast *P*/*M* and *E*/*Z* isomerization in the primary step that is followed by a slower thermal *M*/*P* isomerization (Scheme 7). The thermal isomerization of the *M*,*Z* to the *P*,*Z* stereoform is driven by an unfavorable 1,3-allylic strain in the *M*,*Z* form between the equatorial OH group and the lower part of the molecule, as can be seen from the depiction of the *M*,*Z* half-chair conformer in Scheme 7. An inversion of the half-chair results, leading to *M*/*P* isomerization to the *P*,*Z* isomer. The same is true for the thermal *M*,*E* isomerization to the *P*,*E* isomer after photochemical isomerization of the *P*,*Z* form. Thus, as has been shown before, alkenes of type **1–3** can be used as unidirectional molecular rotors.[8] Unsubstituted alkenes (R = H) show only two isomers whereas substituted switches can adopt four stereoisomeric forms. In the case of the unsubstituted switches, the *P* and *M* diastereomers show a distinct difference between the two diastereomeric forms, providing good contrast and sensitivity for monitoring the switching process. In general, this was also the case with the substituted switches, even though large differences in the overall change of the spectral shape were observed from system to system. The *E* and *Z* diastereomers of **2c** and **3c** showed no difference in their absorption spectra. This was confirmed by comparing the absorption spectrum of diastereopure (*P*,*E*)-**2c** and (*P*,*E*)-**3c** with a spectra of the corresponding *E*/*Z* mixtures. Also, no change in the isosbestic points was observed during the photoinduced switching and ensuing thermal isomerization (see below). Moreover, the spectra of the *E* and *Z* diastereomers of the other alkenes **2** and **3** showed only a small or no difference.

In our investigations of the substituted alkenes **2** and **3**, first the effect of the electron-withdrawing and -donating groups on the absorption spectra was determined. For comparison, the previously synthesized unsubstituted switches **2f** and **3f** were included.[9] Each spectrum was normalized to the global maximum at around 360 (**2a–f**) or 325 nm (**3a**,**c**,**f**). Both the positions of the absorption maxima and the overall shapes of the spectra were correlated with the electronic nature of the substituents (Figure 1 and Figure 2, also see Table S1 and Figure S1 in the Supporting Information).

It was shown that the strongest influence on the absorption spectra stems from the nature of the bridging group in the upper part of the molecule. The oxygen-bridged compounds **2a–f** show a global maximum at around λ_{max} = 355 nm with some smaller, additional peaks at around 320 nm. For the methylene-bridged alkenes **3a**,**c**,**f**, however, only one main band near λ_{max} = 325 nm is visible, probably due to an overlap with other absorption bands at even shorter wavelengths.

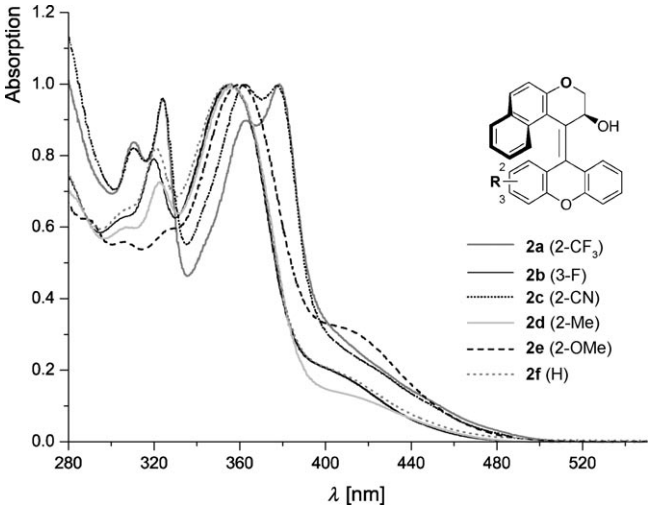


Figure 1. UV/Vis absorption spectra of the oxygen-bridged alkenes **2a–f**. A colored version is provided in the Supporting Information.

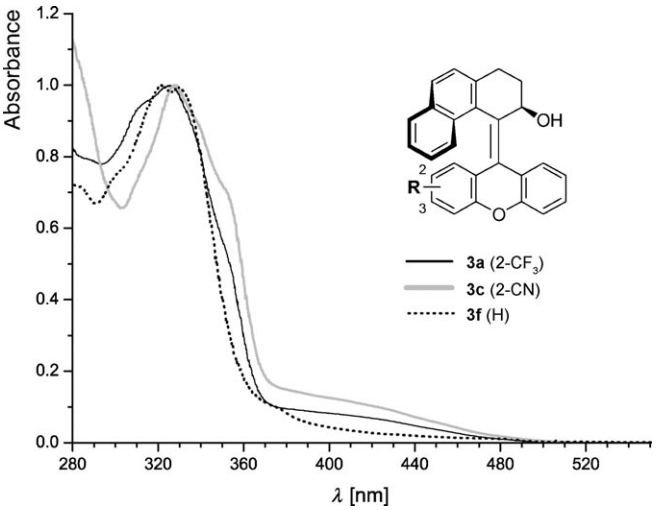


Figure 2. UV/Vis absorption spectra of the methylene-bridged alkenes **3a**,**c**,**f**.

Systematic trends can be observed when comparing the positions and the changes in the shapes of the steady-state absorption bands of the compounds with either donor or acceptor substituents on the lower ring. For instance, in the case of alkenes **2**, the main band (330–400 nm) in the UV spectra of compounds **2a**,**c**, which feature electron-withdrawing substituents at the 2-position of the lower part, shows a double-peak structure and is shifted to longer wavelengths by around 20 nm relative to the unsubstituted compound (**2f**). On the other hand, with electron-donating substituents (**2d**,**e**) a structureless broad band is observed and the absorption maxima and the band width are only slightly different from **2f**. Note that **2b** is a special case, because it is the only compound with substitution at the 3-position of the lower part: Interestingly, although it bears the electron-withdrawing fluorine as substituent, its absorption spectrum is similar to that of the unsubstituted compound (**2f**) and those of compounds with electron-donating substituents at the 2-position (**2d**,**e**). In future studies it will therefore be worthwhile investigating how an electron donor at the 3-position of the lower part affects the spectral properties. For the alkenes **3**, compared with the unsubstituted congener (**3f**), changes in the absorption spectra of the main bands are considerably smaller, but the tail region at around 375 nm also appears to shift somewhat towards longer wavelengths when an electron-withdrawing substituent (**3a**,**c**) is introduced.

In addition, the effect of the substituent on the switching properties of each alkene was studied qualitatively. For this, each compound was irradiated with light in the wavelength range $310 < \lambda_1 < 365$ nm (see the Experimental Section for details) and the absorption spectra were recorded until the photostationary state was reached (the changes are summarized in Table 4). The wavelength range chosen includes the absorption maxima of all the investigated compounds **2** and **3**.[19] Each spectrum was normalized to the maximum at around 360 (**2a–e**) or 325 nm (**3a**,**c**) prior to light irradiation and all later spectra were referenced to the first measurement. Figure 3 shows a representative example for **2d** (further spectra can be found in the Supporting Information). The absorption spectrum of the pure *P* form has a shoulder at around 420 nm. Upon irradiation at $310 < \lambda_1 < 365$ nm, a band centered at around 400 nm grows up with time, which arises from the *M* form produced by the switching process. At the same time, the characteristic band of the *P* form, with a peak at around 360 nm, decays. After a characteristic irradiation time, a photostationary equilibrium is reached. We note that there is a clean isosbestic point at around 370 nm, which indicates the transformation between the two species *P* and *M*.

Table 4. Quantitative change in absorbance ΔA of UV/Vis spectra after irradiation.

Switch (X,R)	Absorbance change[a]					
	λ_a [nm]	ΔA	λ_b [nm]	ΔA	λ_c [nm]	ΔA
2a (O,CF_3)	–[b]	–	–[b]	–	–[b]	–
2b (O,F)	320	−0.21	356	−0.28	389	+0.758
2c (O,CN)	324	−0.03	363	−0.06	379	+0.06
					407	+0.17
2d (O,Me)	323	−0.19	356	−0.36	394	+0.76
2e (O,OMe)	–[c]	–	359	−0.37	400	+0.77
3a (CH_2,CF_3)	326	−0.13	–[c]	–	–[c]	–
3c (CH_2,CN)	328	−0.02	350	−0.02	380	+0.01

[a] The absorption of the pure *P* isomer was normalized. The probe was irradiated until the photostationary state was reached. λ_a corresponds to characteristic changes in the absorption spectra in the region 315–330 nm, λ_b corresponds to 350–365 nm, and λ_c to 375–400 nm. [b] No change in the absorption was observed under irradiation. [c] No characteristic changes were observed in this region.

Interestingly, the switching behavior also appears to change systematically with substitution on the lower part. For alkenes **2**, the compounds with electron-donating substituents (**2d**,**e**) or without substitution (**2f**) at the 2-position

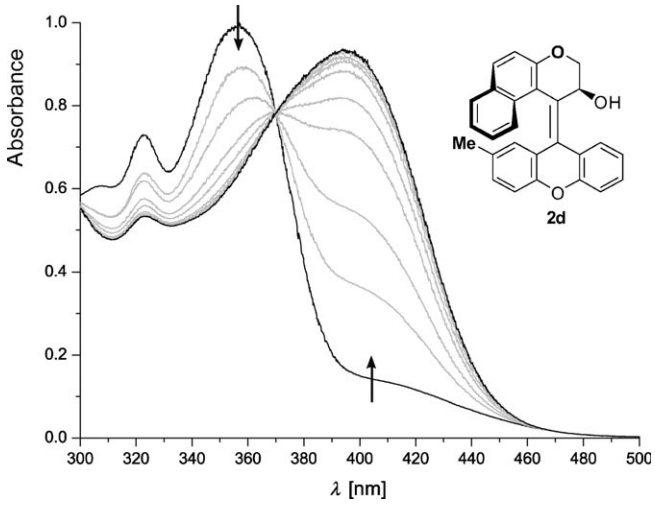


Figure 3. Evolution of the absorption spectra of **2d** in acetonitrile between 300–500 nm upon irradiation at $310<\lambda_1<365$ nm. The black lines represent the start and end states with the grey lines being intermediate measurements recorded every 0.4 min. The arrows depict the increase or decrease in absorbance over time.

show pronounced switching behavior. In contrast, electron-withdrawing substituents lead to either slightly less pronounced changes, as in the case of **2c**, or no change, as for **2a**. Factors influencing the relative absorption ratios are the specific concentrations of the two forms in the photostationary equilibrium and their difference in oscillator strength. The reason for the special behavior of **2a** is as yet unclear: One possible explanation for the apparently inefficient switching in **2a** or **2c** could be the intramolecular interaction between the electron-withdrawing group and the upper part and further experiments will be required to address this issue, for example, spectroscopic studies of the switching process on short timescales. For instance, it could be that isomerization is suppressed by a competing nonradiative pathway after electronic excitation. Alternatively, the timescale for the thermal back-reaction after switching could be considerably faster than for the other compounds such that the concentration of the isomer in the photostationary state of the current experiments is very low. The switch with a substituent at the 3-position (**2b**) behaved very much like **2d–f**, consistent with the absorption band characteristics above. Alkenes **3** displayed only small changes with and without substitution.

After the qualitative investigation, the kinetics of the switching and usually more than one switching cycle were studied to monitor the fatigue resistance of the systems. The monitoring under thermal conditions involved recording the time-dependent absorption changes of the sample at 300 K in the absence of light. According to their photochemical and thermal switching behavior, we have grouped the compounds into three categories: 1) Completely photochemically and thermally reversible ("normal" switching), 2) photochemically reversible, thermally only partially reversible, and 3) neither photochemically nor thermally reversible. It is, however, important to note that the "irreversible" switching led, under either thermal conditions or irradiation, to an incomplete reversion from the photostationary state back to the pure *P* stereoisomer. An intermediate of so far unknown structure is formed that thermally reverts back to the corresponding *P* stereoisomer overnight. In all cases, no degradation of the molecules during the switching process was observed (Figures 4–6 and Table 5, additional spectra in the Supporting Information).

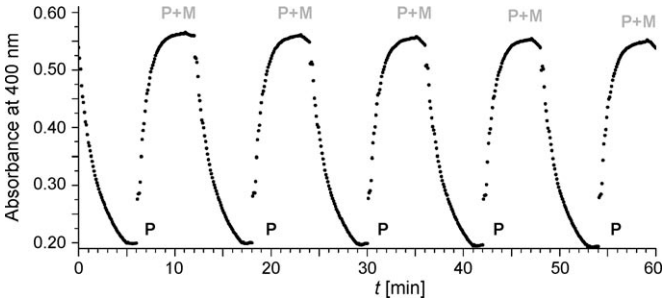


Figure 4. Fully reversible switching of **3f** under alternating irradiation with light of $310<\lambda_1<365$ and $400<\lambda_2<445$ nm.[9]

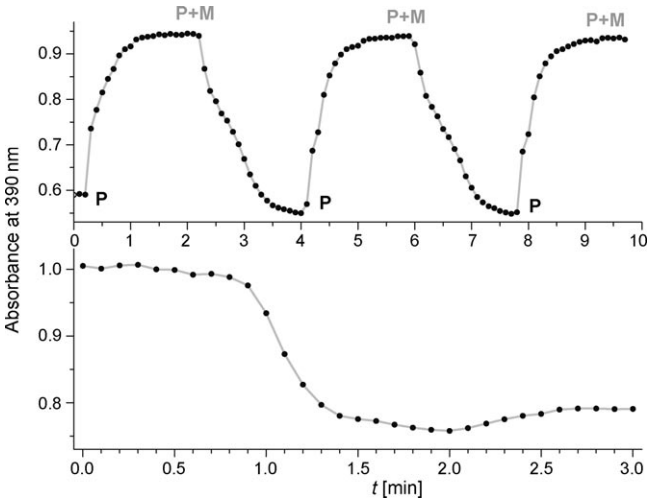


Figure 5. Photochemical reversible switching of **2b** under alternating irradiation with light of $310<\lambda_1<365$ and $400<\lambda_2<445$ nm. The lower graph shows the incomplete reversion in the absence of light.

Summarizing, the introduction of substituents led to a drastic change in the switching behavior of the helical alkenes. The most obvious aspect is the reversibility of the overall process and in the case of **2a** the absence of any changes. Alkenes **2b**, **2c**, and **3c** show full reversibility upon alternating irradiation with light of two different wavelengths ($310<\lambda_1<365$ nm, $400<\lambda_2<445$ nm). The photoinduced *P*/*M* isomerization occurred under the chosen conditions in the order of minutes, however, depending on the choice of substituent, the photostationary state was reached between 1.9 (**2b**) and 8 min (**2d**). No clear trend in the time

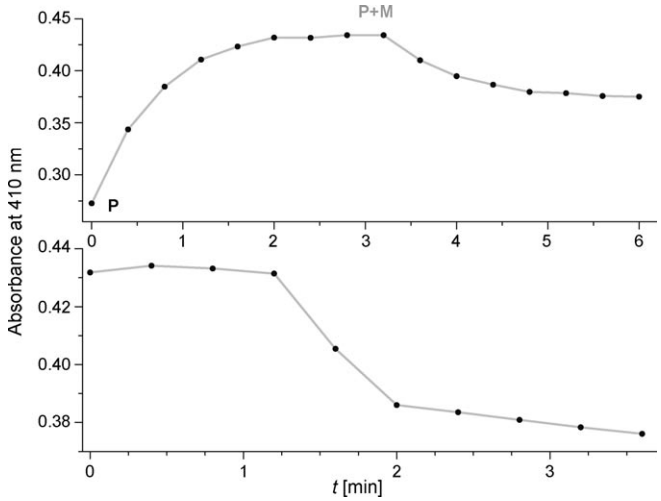


Figure 6. Photochemical irreversible switching of **2c** under alternating irradiation with light of $310<\lambda_1<365$ and $400<\lambda_2<445$ nm. The lower graph shows the incomplete reversion in the absence of light.

Table 5. Measured kinetics and overall switching behavior.

Switch (X,R)	λ[a] [nm]	t[b] [min]	Switching
2a (O,CF_3)	–	–	no spectral changes observed
2b (O,F)	389	1.9	normal switching behavior under irradiation, thermally irreversible
2c (O,CN)	410	3.2	normal switching behavior under irradiation, thermally irreversible
2d (O,Me)	394	ca. 8	neither photochemically nor thermally reversible
2e (O,OMe)	400	3.6	neither photochemically nor thermally reversible
2f (O,H)	400	6.0	normal behavior[c,d]
3a (CH_2,CF_3)	325	3.6	normal behavior[c]
3c (CH_2,CN)	328	2.8	normal switching behavior under irradiation, thermally irreversible
3f (CH_2,H)	380	6.0	normal behavior[c,d]

[a] Wavelength chosen for monitoring of the switching. [b] Time until the photostationary state was reached. [c] Completely photochemically and thermally ($T=300$ K) reversible. [d] The data is taken from ref. [9].

required to reach the photostationary state could be found with respect to the nature of the substituent.

The thermal reversion, whether complete or incomplete, occurs for the systems **2a–e** and **3a**,**c** in the order of minutes. Even though some alkenes show good contrast between the pure *P* stereoisomer and the *P*/*M* mixture in the photostationary state (**2b**,**d**,**e**), the partial irreversibility and the fast thermal isomerization step prevents their usage in optical data storage devices. Although alkene **3a** might potentially be used, the maximum contrast is, however, smaller than for the unsubstituted alkenes **2f** and **3f**.

As already mentioned, the intermediate observed in the back-switching of **2b–e** and **3c** has not been characterized so far. A metastable electronic state is unlikely due to the longevity of the observed intermediate. It is possible that a metastable conformer, for example, a boat conformer, could account for the recorded data. However, further measurements will be required to give clues as to the nature of that state.

In any case, variation of the type and position of the substituents on the lower part of these compounds leads to an impressive variability of the steady-state and dynamic absorption properties. The effect of substituents on the photochemical properties make this class of compound an attractive target for in-depth studies of the switching process on very short timescales. Such experiments are currently underway in our laboratories. These will provide information regarding the molecular switching-mechanism and the substituent-dependence of the ultrafast photoinduced kinetics. Such mechanistic information will be prerequisite to the tailoring of chiroptical switches with higher optical contrast and improved thermal stability.

Conclusion

We have described the successful expansion of the diastereoselective domino carbopalladation/Stille reaction for the construction of various acceptor- (CF_3, F, CN) and donor-substituted (Me, OMe) helical alkenes **2** and **3**. It has been shown that, depending on the electronic nature of the substituent, the reaction proceeds by two complementary methods using either P*t*Bu_3·HBF_4 or IPr·HCl (**23**) as the ligand. In addition to oxygen-bridged alkenes, two methylene-bridged systems were synthesized.

The photophysical properties of all the substituted helical alkenes were investigated. The UV/Vis absorption spectra were mainly influenced by the bridging group. The electron-donating or -withdrawing properties of the lower part of the molecule led to some differences in the steady-state spectra and significant changes in the switching behavior. Thus, the time to reach photostationary equilibrium, the reversibility of the process, and possibly also the probability of competing nonradiative pathways greatly depend on the type of substituent.

Thus, the peculiar substituent effect on both the domino reaction and the photochemical properties makes this class of compound very attractive for further studies.

Experimental Section

Full synthetic details and general procedures for all the synthesized compounds **2a–e**, **3a**,**c**, **4a–e**, **5a–e**, **6**, **7**, **8a–e**, **9–13**, **16a–e**, **17b**,**d**,**e**, **18b**,**d**,**e**, **19a–e**, **20a–e**, **21**, and **22a–d** can be found in the Supporting Information.

Representative procedure for the alkynylation in the synthesis of 4d: NEt_3 (46 mg, 63 μL, 0.456 mmol, 10.00 equiv) was added to a solution of LiHMDS (68 μL, 0.068 mmol, 1.50 equiv, 1.00 M in toluene) at −78 °C followed by the addition of a solution of the alkyne **8d** (34 mg, 0.068 mmol, 1.50 equiv) in toluene (0.6 mL). The reaction solution was stirred at −78 °C for 15 min, at −60 °C for 15 min, allowed to reach RT over 30 min, and stirred at RT for another hour. After cooling back to −78 °C, a solution of the aldehyde **6** (19 mg, 0.071 mmol, 1.00 equiv) in toluene (1.5 mL) was added through a syringe pump over 10 h and the mixture was stirred at −78 °C for another 5 h. Afterwards, the solution was allowed to reach RT over 3 h and the reaction was stopped by the addition

of a sat. aq. solution of NH_4Cl (5 mL) and H_2O (5 mL). The aqueous phase was extracted with EtOAc (3×10 mL), the combined organic phases were dried over $MgSO_4$, and the solvent removed in vacuo. Flash column chromatography (SiO_2, PE/EtOAc, 20:1) afforded the alcohol **4d** as a yellow oil (24 mg, 0.030 mmol, 65%).

^{1}H NMR (600 MHz, $CDCl_3$): δ=0.81 (t, J=7.3 Hz, 9H; Sn-[$(CH_2)_3CH_3$]$_3$), 0.96–1.10 (m, 6H; Sn[$CH_2(CH_2)_2CH_3$]$_3$), 1.20–1.29 (m, 6H; Sn[$(CH_2)_2CH_2CH_3$]$_3$), 1.44–1.53 (m, 6H; Sn($CH_2CH_2CH_2CH_3$)$_3$), 2.31 (s, 3H; 4‴-CH_3), 2.80 (s, 1H; 2-OH), 4.19 (ddd, J=17.2, 9.5, 5.5 Hz, 2H; 1-CH_2), 5.01 (dd, J=7.7, 3.2 Hz, 1H; 2-CH), 6.67 (d, J=8.2 Hz, 1H; 3”-CH), 6.78 (dd, J=8.3, 0.8 Hz, 1H; 6‴-CH), 6.99 (td, J=7.6, 1.0 Hz, 1H; 4”-CH), 7.04 (dd, J=8.2, 1.5 Hz, 1H; 5‴-CH), 7.13 (d, J=8.9 Hz, 1H; 3′-CH), 7.21 (ddd, J=9.1, 7.5, 1.7 Hz, 1H; 5”-CH), 7.26 (d, J=1.8 Hz, 1H; 3‴-CH), 7.40 (ddd, J=8.0, 6.9, 1.0 Hz, 1H; 6′-CH), 7.48 (dd, J=7.7, 1.6 Hz, 1H; 6”-CH), 7.54 (ddd, J=8.3, 6.8, 1.2 Hz, 1H; 7′-CH), 7.73 (d, J=8.1 Hz, 1H; 4′-CH), 7.77 (d, J=8.8 Hz, 1H; 5′-CH), 8.11 ppm (d, J=8.5 Hz, 1H; 8′-CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ=10.0 (Sn-[$CH_2(CH_2)_2CH_3$]$_3$), 13.8 (Sn[$(CH_2)_3CH_3$]$_3$), 20.8 (4‴-Me), 27.4 (Sn-[$(CH_2)_2CH_2CH_3$]$_3$), 29.2 (Sn($CH_2CH_2CH_2CH_3$)$_3$), 62.2 (C-2), 74.2 (C-1), 82.6 (C-4), 89.5 (C-3), 90.1 (C-1′), 113.6 (C-1“), 115.0 (C-3′), 116.8 (C-3”), 117.6 (C-6“), 122.4 (C-4”), 124.7 (C-6′), 128.1 (C-4′, C-7′), 129.9 (C-5“), 130.2 (C-5‴), 130.3 (C-5′), 131.2 (C-8′), 132.4 (C-8′a), 132.6 (C-2“′), 133.9 (C-6”, C-4“′), 135.4 (C-4′a), 137.8 (C-3‴), 155.3 (C-2′), 158.4 (C-2“), 159.0 ppm (C-1‴); IR (film): ν=3418, 2955, 2924, 2870, 2852, 1594, 1464, 1252, 1211, 1074, 749 cm^{-1}; UV (CH_3CN): λ_{max} ($\log\varepsilon$/M^{-1}cm^{-1})=203.5 (4.7753), 233.0 (4.8661), 285.0 (3.9660), 323.0 (3.3766), 335.5 nm (3.3816); MS (ESI, MeOH): m/z (%): 1641.3 (77) [2M+Na]$^+$, 833.1 (100) [M+Na]$^+$; HRMS (ESI): m/z calcd for $C_{39}H_{47}IO_3Sn$ [M+Na]$^+$: 833.1492; found 833.1498.

Representative procedure for the domino carbopalladation/Stille reaction in the synthesis of 2d: A mixture of [Pd_2dba_3] (0.6 mg, 0.001 mmol, 0.05 equiv), PtBu$_3$·HBF$_4$ (0.4 mg, 0.001 mmol, 0.10 equiv), and CsF (4.0 mg, 0.027 mmol, 2.20 equiv) in dioxane (0.2 mL) was stirred at RT for 5 min and then a solution of **4d** (9.5 mg, 0.012 mmol, 1.00 equiv) in dioxane (0.6 mL) was added. The reaction vessel was placed in a preheated oil bath at 80°C and stirred for 18 h. Afterwards, the mixture was cooled to RT and the reaction quenched by the addition of a sat. aq. solution of NH_4Cl (5 mL) and H_2O (5 mL). After the extraction with EtOAc (3×10 mL), the organic phase was dried over $MgSO_4$ and the solvent removed in vacuo. Purification by flash column chromatography (SiO_2, PE/EtOAc 20:1) yielded **2d** as a yellow resin as a 1:1 mixture of the E and Z stereoisomers (3.0 mg, 0.008 mmol, 67%).

^{13}C NMR[20] (125 MHz, $CDCl_3$): δ=20.1 (Z-CH_3), 21.2 (E-CH_3), 65.1 (E-C-2, Z-C-2), 74.3 (E-C-3, Z-C-3), 113.8 (E-C-10b), 113.9 (Z-C-10b), 115.9 (Z-C-3′), 116.4 (Z-C-5), 116.6, 116.9 (Z-C-5′), 118.0, 118.0, 122.4 (E-C-7′), 122.9, 122.9, 123.1 (Z-C-3′), 123.2, 124.1, 124.2, 124.2, 124.3, 124.5, 125.1, 125.5, 125.6, 125.7 (Z-C-8), 125.8 (E-C-8), 127.3 (Z-C-8′), 127.4, 127.5 (E-C-8′), 127.6, 127.8, 128.0 (Z-C-1′), 128.0 (E-C-6′), 128.6 (Z-C-4′, Z-C-6′), 129.2, 129.2, 129.4, 130.2 (E-C-6), 130.4 (Z-C-6), 130.6, 130.7, 131.9, 132.5, 151.1, 152.4, 153.3, 154.0, 154.0, 154.5 ppm; UV (CH_3CN): λ_{max} ($\log\varepsilon$/M^{-1}cm^{-1})=226.0 (4.5158), 307.0 (3.5843), 322.5 (3.6628), 356.0 nm (3.7936); MS (ESI, MeOH): m/z (%): 807.3 (100) [2M+Na]$^+$, 415.1 (97) [M+Na]$^+$; HRMS (ESI): m/z calcd for $C_{27}H_{20}O_3$[M+Na]$^+$: 415.1305; found: 415.1295.

E stereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ=1.74 (d, J=7.0 Hz, 1H; 2-OH), 2.41 (s, 3H; 2′-CH_3), 4.70–4.80 (m, 2H; 3-CH_2), 5.83 (s, 1H; 2-CH), 6.29 (ddd, J=8.1, 7.4, 1.3 Hz, 1H; 7′-CH), 6.52 (dd, J=7.9, 1.4 Hz, 1H; 8′-CH), 6.91–6.96 (m, 2H; 6′-CH, 8-CH), 7.10 (m_c, 1H; 9-CH), 7.15 (dd, J=8.2, 1.0 Hz, 1H; 5′-CH), 7.16 (d, J=8.9 Hz, 1H; 3′-CH), 7.19–7.24 (m, 4H; 1′-CH, 4′-CH, 7-CH, 5-CH), 7.63 (d, J=8.1 Hz, 1H; 10-CH), 7.71 ppm (d, J=8.8 Hz, 1H; 6-CH). Z stereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ=1.52 (s, 3H; 2′-CH_3), 1.77 (d, J=6.6 Hz, 1H; 2-OH), 4.70–4.80 (m, 2H; 3-CH_2), 5.85 (s, 1H; 2-CH), 6.28 (d, J=1.7 Hz, 1H; 1′-CH), 6.73 (ddd, J=8.3, 2.1, 0.6 Hz, 1H; 4′-CH), 6.91–6.96 (m, 1H; 8-CH), 7.04 (d, J=8.2 Hz, 1H; 3′-CH), 7.10 (m_c, 1H; 9-CH), 7.17 (d, J=8.8 Hz, 1H; 5-CH), 7.19–7.24 (m, 2H; 7′-CH, 7-CH), 7.29 (dd, J=8.1, 1.2 Hz, 1H; 5′-CH), 7.35 (ddd, J=8.3, 7.2, 1.5 Hz, 1H; 6′-CH), 7.43 (dd, J=7.7, 1.5 Hz, 1H; 8′-CH), 7.63 (d, J=8.1 Hz, 1H; 10-CH), 7.72 ppm (d, J=8.8 Hz, 1H; 6-CH).

Optical experiments: A commercial absorption spectrometer (Varian Cary 50 Bio) was employed to record the steady-state absorption spectra and the photoinduced switching processes. In a typical switching experiment a sample of (*P,E*)-**2/3** was subjected to light at alternating wavelengths. A high-pressure Hg/Xe Lamp (Osram HBO, 200 W) combined with appropriate optical glass filters (Schott) was used. For irradiation in the wavelength range $310<\lambda_1<365$ nm we employed a UG11 (thickness: 1 mm) and WG320 (2 mm) filter combination. They acted as a bandpass filter so that only the Hg lines at 313.2, 334.1, and 365.0 nm were used for illumination. The light was focused on the sample cell by a Suprasil I lens with a focal length of 100 mm. The new absorption band emerging at longer wavelengths was attributed to the absorption of the switched form. At the same time the original band at short wavelength decreases. Back-switching was induced by using the same lamp in combination with a GG400 (1 mm) filter. This filter provides a sharp cut-off below 400 nm and therefore only the Hg lines at 404.6 and 435.8 nm can pass, which are located in a spectral region in which the switched form predominantly absorbs. The power of the filtered light was measured at the sample position by using a calibrated power meter (Melles Griot 13PEM001): The power was 23 mW for the UG11/WG320 filter combination and 190 mW for the GG400 filter.

Acknowledgements

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[19] Because a Hg/Xe lamp was used as the light source yielding a broad wavelength range, filter combinations were chosen to select the desired wavelengths. Monochromators would have lowered the light intensity too much leading to a much slower switching and were thus not used.

[20] The signals of the ^{13}C NMR spectrum could not be fully assigned to the respective *E* and *Z* stereoisomers due to multiplets in the ^{1}H NMR spectrum. The given signals are those of both forms with an assignment given if possible.

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