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Synthesis of Chiroptical Molecular Switches by Pd-Catalyzed Domino Reactions

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Abstract: New photochromic switches based on helical alkenes can quickly and efficiently be accessed by Pd-catalyzed domino reactions using a modular approach; this allows a wide variability in product formation with the advantages of a convergent synthetic route. The alkenes have been synthesized in excellent enantioselectivity and their switching properties assessed by stimulation with nanosecond laser pulses at two different wavelengths in over 1000 switching cycles.

Introduction

The development of organic compounds that allow a controlled motion at the molecular level is an important prerequisite for the construction of nanoswitches and nanomotors.[1,2] Based on today's requirements in the miniaturization of data storage devices and the concomitant success of digital optical data systems, in which recording and read-out of information is carried out by light, the shift from classic electronic semiconductor elements to light-driven molecular switches has gained great impetus. This is underlined by the development of new information storage techniques, fabrication processes and novel synthetic methodologies in the past years.[3]

The advantage in using inorganic compounds for data-storage devices is the long-term knowledge and experience of their fabrication, but they lack some desirable properties such as. e.g. the fine-tuning of a large variety of physical properties or the characterization of single isolated structures. On the other hand, organic compounds can overcome such deficiencies with the embedded advantage of solving problems such as decreased thermal and photochemical stability by small structural modifications.

The basic requirement for a molecular switch is bistability, in which both forms can be interconverted by means of external stimuli such as light, heat, pressure, magnetic or electric fields, pH change or chemical reactions.[2a,4] Moreover, one must be able to selectively address both forms individually and detect them separately, preferably on very short time scales to allow their potential use in modern computing machines.[5]

The chiroptical switches developed by Feringa et al. (e.g., **1**) containing a helical tetra-substituted alkene moiety are particularly promising since their stable states can be accessed using circularly polarized light (Scheme 1).[6]

Quite recently, tetra-substituted alkenes have also been prepared by Lautens, Florent and Yu.[7]

Here we describe an efficient and general access to novel compounds of type **2** with a helical backbone using Pd-catalyzed

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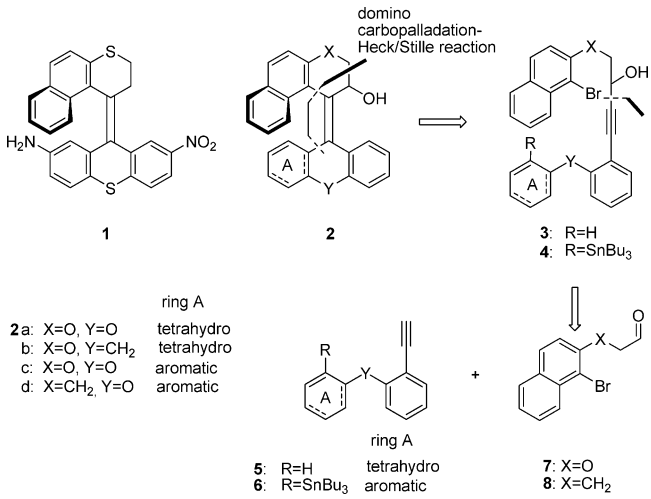
Scheme 1. Chiroptic Molecular Switches **1** and **2**



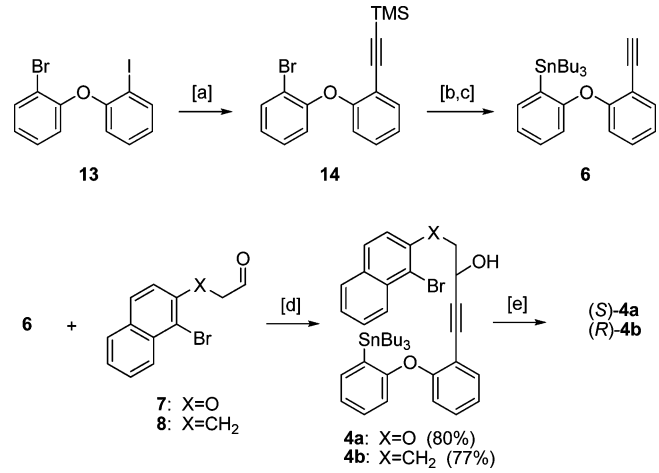
domino processes[8] consisting either of a carbopalladation of an alkyne and a Mizoroki−Heck reaction or a combination of a carbopalladation and a Stille reaction.

Results and Discussion

Synthesis of the Substrates 3a,b and 4a,b. As precursors for the formation of the tetra-substituted alkenes **2a**−**d** compounds **3a** and **3b** with a cyclohexene moiety as ring A as well as **4a** and **4b** with an aromatic ring A were employed, which could easily be obtained by addition of the metalated alkynes **5a** and **5b** as well as **6** to the aldehydes **7** and **8**, respectively.

The synthesis of **5a** was accomplished by coupling 3-bromocyclohexene (**9**) and *o*-iodophenol (**10**) under basic conditions followed by a Sonogashira reaction with propargylic alcohol and subsequent oxidative removal of the hydroxymethyl group employing MnO_2 (Scheme 2). In a similar way, **5b** was synthesized by reaction of **11** with **9** followed by the introduction of the alkyne moiety. After metalation of **5a** and **5b** and subsequent coupling with aldehyde **7**[9] compounds **3a** and **3b** were obtained in 91% and 82% yield, respectively, as an almost 1:1 mixture of diastereomers, which could be separated by chromatography on silica gel. For the preparation of the enantiopure helical alkenes **2a**−**b** the enantiomers of **3a** and **3b** were separated by HPLC on a chiral stationary phase.[10]

Scheme 3. Synthesis of **4a** and **4b**[a]



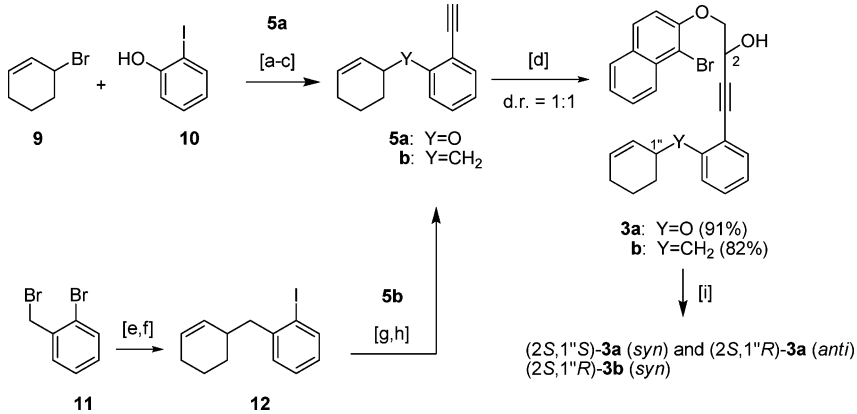
[a] Reagents and conditions: (a) Me_3SiCCH, $PdCl_2(PPh_3)_2$, CuI, NEt_3, RT, 18 h, 92%; (b) *t*BuLi, Bu_3SnCl, THF, −78 °C→RT, 1.5 h, 92%; (c) K_2CO_3, $MeOH/CH_2Cl_2$, RT, 12 h, 97%; (d) LiHMDS, NEt_3, toluene, −78 °C, 18 h; (e) chromatography on a chiral stationary phase support (Daicel IB), >99% *ee*.

The synthesis of the substrates **4a** and **4b** for the preparation of the tetra-substituted alkenes **2c** and **2d** containing an aromatic A ring by a domino carbopalladation/Stille reaction[11] was carried out employing the known diphenyl ether **13** as starting material that is accessible from *o*-bromophenol and *o*-fluoronitrobenzene in three steps.[12] Sonogashira coupling of **13** with TMS acetylene gave **14**, which by a lithium-halide exchange and subsequent transmetalation and desilylation in basic methanol led to **6** in three steps in 82% yield (Scheme 3). The coupling of **6** with the aldehydes **7** and **8**[9,13] to give **4a** and **4b** was achieved in 80% and 77% yield, respectively, employing LiHMDS as base and NEt_3 as complexing additive in toluene and slow addition of the aldehyde. The use of *n*BuLi, LDA and KHMDS as bases only caused a polymerization of the aldehyde.

There is a high solvent dependence in this reaction which is attributed to the aggregation behavior of organolithium compounds,[14] while the slow addition of the aldehyde prevents an aldol condensation.

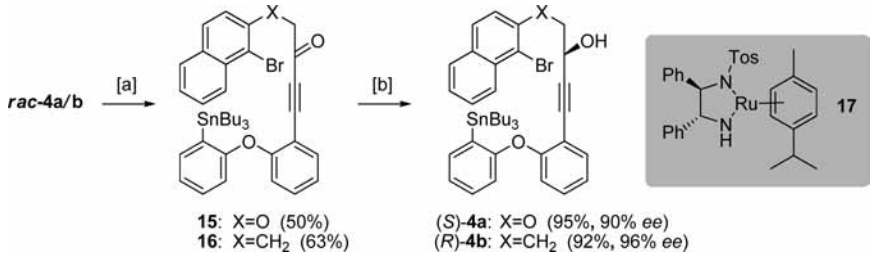
For the preparation of the enantiopure helical alkenes **2c**−**d** the racemic alcohols **4a** and **4b** were resolved by HPLC on a chiral stationary phase with >99 ee;[10] however, they were also

Scheme 2. Synthesis of Substrates **3a,b**[a]



[a] Reagents and conditions: (a) K_2CO_3, DMF, 80 °C, 1 h, 98%; (b) propargylic alcohol, $PdCl_2(PPh_3)_2$, CuI, $HNiPr_2$, RT, 19 h; (c) MnO_2, KOH, Et_2O, RT, 1 h, 75% over 2 steps; (d) *n*BuLi, **7**, THF, −60 °C→RT, 4 h; (e) Mg, **9**, Et_2O, RT, 12 h, 63%; (f) *t*BuLi, I_2, Et_2O, −78 °C→0 °C, 2 h, 80%; (g) propargylic alcohol, $PdCl_2(PPh_3)_2$, CuI, NEt_3, THF, RT, 24 h; (h) MnO_2, KOH, Et_2O, RT, 1 h, 64% over 2 steps; (i) chromatography on silica gel and chromatography on a chiral stationary phase (Daicel IB), >99% ee.

Scheme 4. Enantioselective Synthesis of **4a** and **4b**[a]



[a] (a) Dess−Martin periodinane, CH_2Cl_2, RT, 15 h; (b) **17**, *i*PrOH, MeCN, RT.

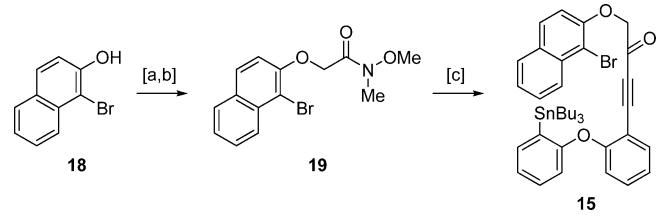
prepared in an enantioselective way by reduction of the corresponding ketones **15** and **16**, respectively, using the chiral Noyori catalyst **17**[15] in a transfer hydrogenation to give (*S*)-**4a** and (*R*)-**4b** with excellent yield and very good enantioselectivity of 90 and 96% ee (Scheme 4). For the enantioselective reduction of **15** we also investigated DIP-Chloride[16] and Me-CBS.[17] Whereas DIP-Chloride only led to a decomposition of **15**, CBS-reduction gave enantioenriched **4a** with moderate 40% ee.

The ketones **15** and **16** were obtained by oxidation of the racemic alcohols **4a** and **4b** using Dess−Martin periodinane with 50% and 63%, respectively. Both with IBX and pyridine·SO_3 according to Parikh−Doering[18] an oxidation was not possible; employing Swern conditions a decomposition of the substrates and with MnO_2 only partial conversion was observed.

Besides the oxidation of **4a** to give the ketone **15** we also developed a more straightforward approach in which **15** was directly formed by coupling of **6** with the corresponding Weinreb amide **19** derived from **18** in 55% yield (Scheme 5).

In addition to the preparation of the enantioenriched alcohols **4a** and **4b** by the two-step oxidation−reduction process, we also looked into their direct synthesis by an enantioselective addition of the alkyne **6** on the aldehydes **7** and **8**. There are several ways to perform an enantioselective alkynylation of aldehydes, whereby the two procedures developed by Carreira[19] and

Scheme 5. Synthesis of Ketone **15** via Weinreb Amide **19**[a]



[a] Reagents and conditions: (a) 2-chloroacetic acid, K_2CO_3, DMF, 120 °C, 3 d, 50%; (b) DCC, DMAP, Et*N*i*Pr*$_2$, HN(OMe)Me·HCl, CH_2Cl_2, RT, 18 h, 67%; (c) **6**, LiHMDS, NEt_3, toluene, −78 °C, 18 h, 55%.

Shibasaki[20] show an especially broad substrate scope. Unfortunately, the two aldehydes **7** and **8** are exceedingly base sensitive, and thus, a product formation was not observed using these procedures. Although the alkyne could be reisolated in almost quantitative yield, the aldehyde decomposed under the employed reaction conditions.

Synthesis of the Tetra-Substituted Alkenes 2a−d by a Pd-Catalyzed Domino Process. The Pd-catalyzed transformation of the enantiopure *syn*-diastereomers of (2*S*,1″*S*)-**3a** and (2*S*,1″*R*)-**3b** using catalytic amounts of the Pd-catalyst **21**[21] led to the helical alkenes (2*S*,*P*)-**2a** and (2*S*,*P*)-**2b** respectively in 80 and 92% yield as single diastereomers. However, under the reaction conditions a partial isomerization of the primarily formed double bond was observed to give an approximately 1:1.2 mixture of the corresponding double bond isomers in ring A (Scheme 6).

In contrast, the reaction of the *anti*-diastereomers of **3a** and **3b** in presence of catalytic amounts of **21** did not give the tetra-substituted alkenes but solely led to the acenaphthylenes **20** by CH activation.[8]

The domino reaction of (*S*)-**4a** and (*R*)-**4b** with Pd_2dba_3 in the presence of P*t*Bu_3·HBF_4[22] afforded the helical alkenes (*S*,*P*)-**2c** and (*R*,*P*)-**2d** in 70% and 55% yield, respectively, again as single diastereomers (Scheme 7). Thus, the configuration of the helical structure in the products **2** of the Pd-catalyzed domino reaction of **3a** and **3b** as well as of **4a** and **4b** is controlled by the stereogenic center in the starting materials, whereby the (*S*)-enantiomer exclusively leads to (*P*)-helicity and the (*R*)-enantiomer to (*M*)-helicity.

The induced diastereoselectivity can be explained by an interaction of the Pd-atom and the hydroxyl group in the

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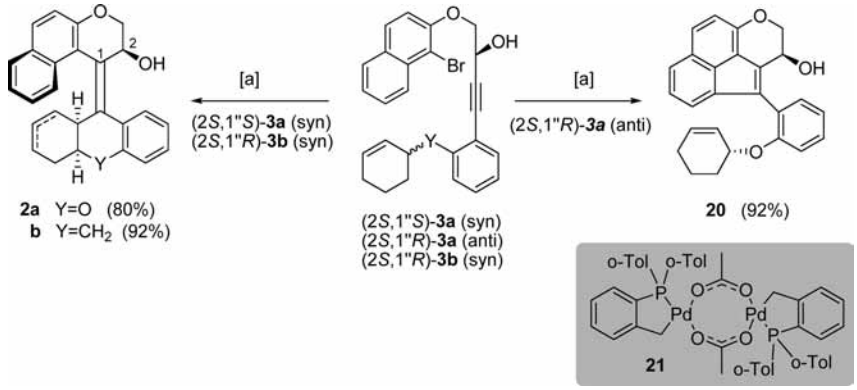
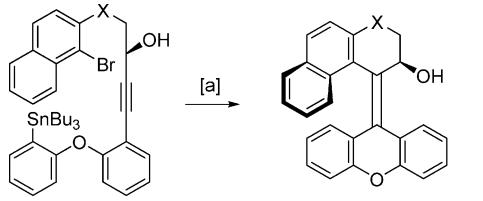
Scheme 6. Domino Reaction of *syn*-**3a**,**b** and *anti*-**3a**[a]



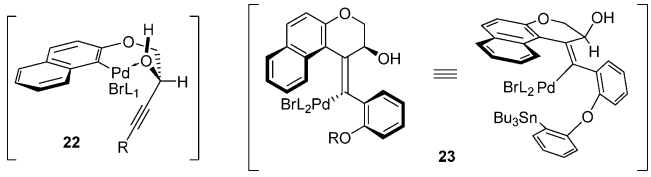
[a] Reagents and conditions: (a) **21**, LiOAc·2 H_2O, tBu_4NOAc, MeCN/DMF/H_2O, 120 °C; *syn*-**3a,b**: 15 h; *anti*-**3a**: 2 h.

Scheme 7. Domino Carbopalladation/Stille Reaction of **4a** and **4b**[a]



[a] Reagents and conditions: (a) Pd_2dba_3, P*t*Bu_3·HBF_4, CsF, 1,4-dioxane, 80 °C, 18 h.

Scheme 8. Proposed Intermediates Explaining the Stereoselectivity in the Domino Carbopalladation/Stille Reaction



primarily assembled Pd-intermediate (**22**),[23] which forces the alkyne moiety to lie below the naphthalene skeleton and thus controls the selective insertion into the triple bond via intermediate **23** (Scheme 8).

For the elucidation of the structures of the helical alkenes **2** compound **2c** was crystallized and its configuration determined by X-ray crystallography (Figure 1, see the Supporting Information for details). The twisted structure of the xanthene moiety in **2c** probably results from a steric hindrance in the *Fjord*-region.[24]

The CD-spectrum of **2c** with its high molar ellipticity of $\Theta = 5 \times 10^5$ deg cm^2 dmol^{-1} indicates that the tetra-substituted alkenes of type **2** contain a chiral chromophore as expected (Figure 2).

Photochemical Investigations. For the determination of the usability of the tetra-substituted alkenes **2** is was necessary to

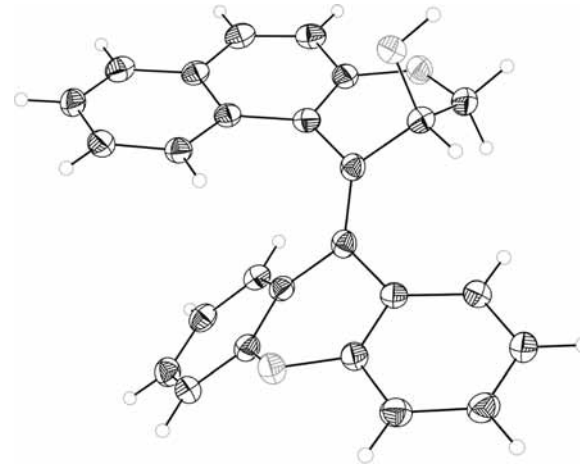


Figure 1. Molecular structure of **2c** in the crystal.

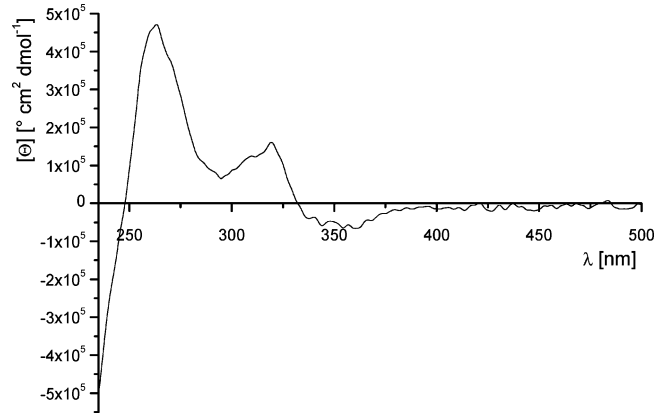


Figure 2. CD spectrum of **2c** in acetonitrile at room temperature.

show that they can exist in two stable configuration which can be interconverted by irradiation with light. Thus, the two diastereomers show drastic differences with respect to their UV−vis absorption spectra in the 300−450 nm range, as shown in Figure 3. For instance, the UV-absorption of the pure **P**-form of **2d** (solid line) shows a λ_{max} only at 325 nm. In contrast, the **M**-form of **2d** (dashed line) is characterized by two absorption bands centered at 320 and 380 nm.

Reversible optical switching was confirmed for both **2c** and **2d** (Scheme 9). First, photophysical investigations were conducted by irradiation of **2c** and **2d** at two wavelength ranges ($310 < \lambda_1 < 365$ nm and $400 < \lambda_2 < 445$ nm) by employing a high-pressure Hg−Xe lamp combined with corresponding

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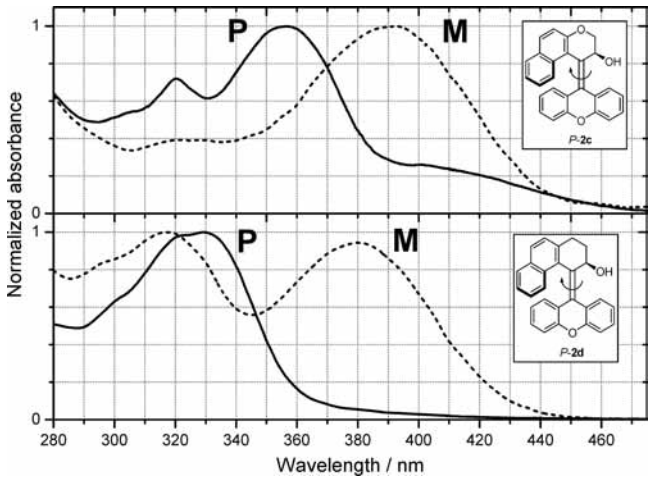
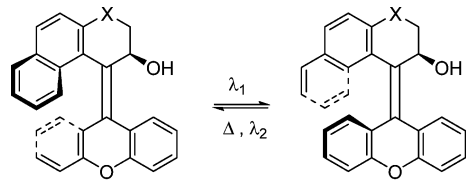


Figure 3. UV−vis spectra of **2c** (upper curve) and **2d** (lower curve). Solid line: **P**-form. Dashed line: **M**-form.

Scheme 9. Light-Induced Interchange Between the Respective **P**- and **M**-Forms of the Aromatic Optical Switches **2c**,**d**



optical glass filters (see the Supporting Information for figures and experimental details). To assess the possibility of a fast optical switching, **2c** and **2d** were subjected to alternate nanosecond laser excitation at wavelengths of 308 and 390 nm employing a repetition frequency of 1 Hz. An instantaneous **P** to **M** conversion was achieved by an excimer laser (308 nm, 15 ns pulse length, 37 mJ·cm^{-2}·pulse^{-1}) and the reverse process was initiated by an excimer-pumped dye laser (390 nm, 15 ns pulse length, 4.6 mJ·cm^{-2}·pulse^{-1}).

The two laser beams were overlapped in a 1 cm quartz cuvette containing a solution of **2c** and **2d** in acetonitrile with an initial optical density of 0.6 for the pure **P**-form. A transient broadband absorption spectrum in the range 314−377 nm was then recorded after each laser shot by monitoring the sample absorption employing a xenon lamp/fiber-coupled spectrograph/gated ICCD combination (with the detection starting 1 μs after the laser shot using a 200 μs integration time). "Non-destructive readout conditions" were achieved by using a fast (∼2 ms opening time) shutter and a suitable glass filter combination placed behind the xenon lamp. This guaranteed that the lamp intensity did not have an impact on the switching process. The thermal **M**→**P** back-conversion of **2d** was found to be negligible during the experiment. It was confirmed that the crossing point at 348 nm (Figure 3, lower panel) is indeed an isosbestic point. Thus, the thermal back-conversion of **2d** takes several hours. In contrast, we observed that **2c** shows inferior thermal stability compared to that of **2d**, and thermal **M**→**P** back-switching occurred on the order of minutes. This is an interesting result, considering the fact that the structural difference between **2c** and **2d** is fairly small.

Each spectrum was normalized to the laser energy and integrated in the regions 314−340 nm ("**P** region") and 360−377 nm ("**M** region"). The results are depicted in Figure 4, A and B, respectively.

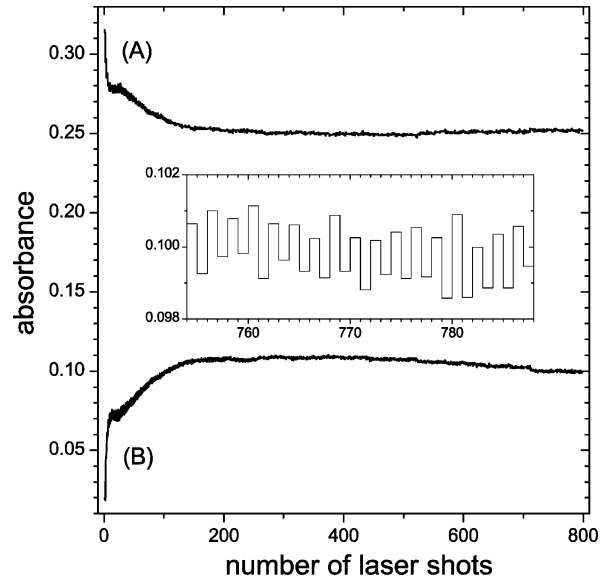


Figure 4. Photochemical switching experiment for **2d** employing alternate 15 ns laser pulses at 308 and 390 nm. Spectra were recorded after each laser shot (repetition frequency 1 Hz) and integrated in the regions 314−340 nm (A) and 360−377 nm (B). The inset shows a magnification of the late part of curve (B) after the establishment of the photostationary equilibrium.

Starting from a solution containing predominantly the **P**-form,[25] it takes approximately 150 alternate laser shots to reach a photostationary equilibrium under the selected conditions: The concentration of **P** decays (curve A) at the expense of **M** (curve B). The inset shows a magnification at long time scales after establishment of the photostationary equilibrium. Characteristic up- and down-steps are observed, which indicate alternate switching from **P** to **M** and vice versa, which is induced by the two different lasers. After 1000 shots no fatigue of the optical switching was observed. Residual drifts of the lines are likely due to an imperfect correction of shot-to-shot fluctuations in the laser energies. The nanosecond laser experiments demonstrate that the light-induced interconversion process between the two diastereomeric isomers is instantaneous and reversible and that **2d** can, in principle, be employed as a reversible optical switch. The distinct change in absorbance between the two diastereomeric isomers of **2d** provides good contrast and sensitivity for monitoring the switching process. However, it is not yet clear which process is responsible for the undulatory structure of the curves A and B at early times before reaching the photostationary equilibrium. This will be dealt with in more detail in future laser spectroscopic investigations.

Conclusions

In conclusion we have described a generally applicable synthetic strategy for the formation of helical tetra-substituted alkenes using a domino reaction that consists of a carbopalladation and a Mizoroki−Heck reaction or a carbopalladation and a Stille reaction. The helical chirality of the tetra-substituted alkenes is controlled by the stereogenic center in the substrates.

(25) The first experiment started with a sample containing only the **P**-form. On subsequent runs the sample had to be converted back to the **P**-form from the **P**/**M**-equilibrium which was achieved by illuminating the sample using a continuous blue-light LED (center wavelength 405 nm, 200 mW) for 30 s prior to the laser experiments.

Broadband transient absorption detection after alternate laser excitation at 308 and 390 nm demonstrates that especially **2d** in principle can be used as an optical switch.

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Note Added after ASAP Publication. The compound numbers corresponding to Scheme 3 were incorrect in the text published ASAP November 13, 2009. The corrected version was published November 19, 2009.

Supporting Information Available: Description of preliminary optical switching experiments, experimental procedures, spectral data, crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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