Helical Structures

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Four- and Sixfold Tandem-Domino Reactions Leading to Dimeric Tetrasubstituted Alkenes Suitable as Molecular Switches**

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Abstract: *A highly efficient palladium-catalyzed fourfold tandem-domino reaction consisting of two carbopalladation and two C–H-activation steps was developed for the synthesis of two types of tetrasubstituted alkenes **3** and **6** with intrinsic helical chirality starting from substrates **1** and **4**, respectively. A sixfold tandem-domino reaction was also developed by including a Sonogashira reaction. 20 compounds with different substitution patterns were prepared with yields of up to 97%. Structure elucidation by X-ray crystallography confirmed helical chirality of the two alkene moieties. Photophysical investigations of some of the compounds showed pronounced switching properties through light-controlled changes of their stereochemical configuration.*

Pseudosymmetric dimeric compounds, which are also found in nature, are interesting substances that very often show dramatic differences in their bioactivity and other properties compared to the corresponding monomeric unit.[1] Their synthesis is usually performed by dimerization of the monomers.[2] On the other hand, a tandem approach in which both parts of the molecule are built up in parallel seems to be much more elegant and efficient. However, only very few examples utilizing this synthetic strategy have been reported to date.[3]

Herein we present a straightforward combination of a tandem approach with our concept of domino reactions[4,5] for the synthesis of dimeric tetrasubstituted alkenes such as **3** and **6** using palladium as catalyst. Transition-metal-catalyzed domino reactions have recently been used by us in the synthesis of functional materials like fluorescent dyes and sterically overcrowded alkenes.[6]

The latter type of compounds was first prepared by Feringa and Wynberg[7] and the use of domino reactions for their synthesis was also described by Lautens et al.[8] and Zhu et al.[9] Sterically overcrowded alkenes have intriguing properties, since they can act as light-driven molecular switches and motors making them suitable for their application as nanodevices in material sciences and biomolecular chemistry as well.

For the synthesis of the novel unusual dimeric tetrasubstituted alkenes **3a** and **6a** with inherent helical chirality we developed a palladium-catalyzed fourfold tandem-domino reaction consisting of two carbopalladation and two C–H-activation reactions starting from substrates **1a** and **4a**, respectively (Scheme 1). Our goal in this field was the design of novel molecules containing two overcrowded alkene moieties, for which the light-driven switching process should be either autonomous or should allow a propeller-like movement where the helicity of the two alkene moieties depends on each other. The concept might also be of interest in view of natural nanomotors.[10]

The first type of molecules would be represented by structure **3a** whereas the second type would be met by structure **6a.** We assume that in the formation of **3a** and **6a** intermediates such as **2a** and **5a** occur, which are formed by two carbopalladation reactions. They then undergo two C–H-activation reactions, probably via transition structures $\mathbf{2a}^{\ddagger}$ and $\mathbf{5a}^{\ddagger}$, with two molecules of acetate.[11] However, exact information about the time sequence cannot be given, though the terminal C–H-activation reactions should be slower due to a higher energy of activation.

For the synthesis of **3a** a combination of $Pd(OAc)_2$ and PPh_3 in a ratio of 1:5 with $(n\text{Bu})_4\text{NOAc}$ as base and the solvent DMF as catalytic system and a catalyst loading of 10 mol% at 100°C under microwave irradiation for 6 h gave the highest yields. Thus, under these conditions **3a**, containing two overcrowded alkene moieties in an *anti* orientation, was obtained from the dialkyne **1a** with 94% yield. Lower catalyst loading with 5 mol% and 1 mol% palladium led to decreased yields as 68% and 2%, respectively. Similarly, for the synthesis of the second type of helical bisalkenes **6a** with a *syn* orientation of the two overcrowded alkene moieties the catalytic system described for **3a** could also be used; however, the reaction time had to be increased to 12 h, which is probably due to much higher strain in molecules of type **6a**. Thus, the process employing dialkyne **4a** again consists of two carbopalladation and two C–H-activation reactions with 10 mol% $Pd(OAc)_2$ and PPh_3 in a ratio of 1:5, $(n\text{Bu})_4\text{NOAc}$

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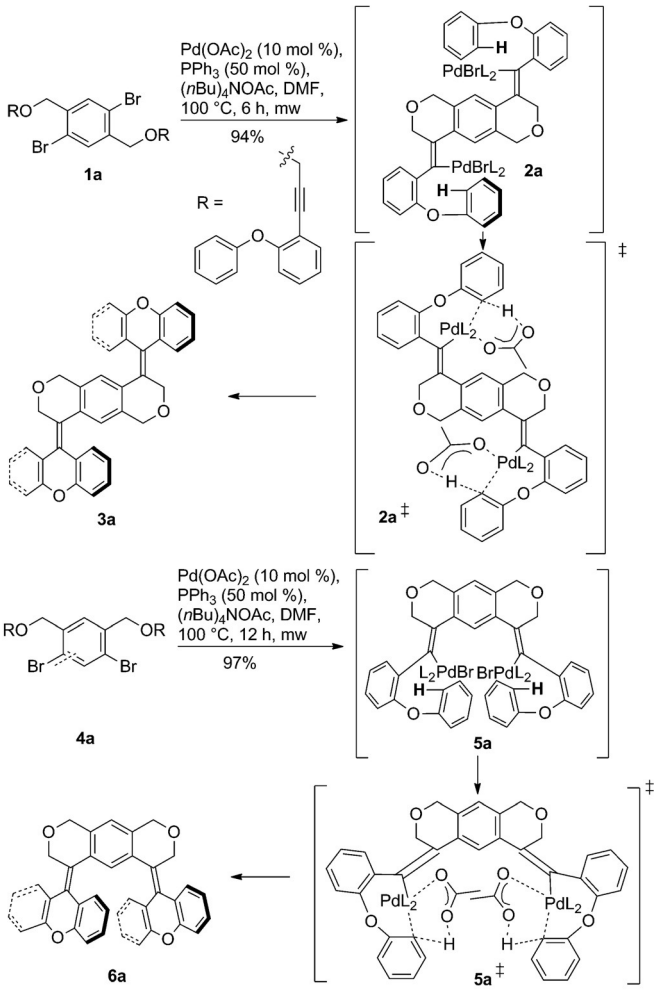
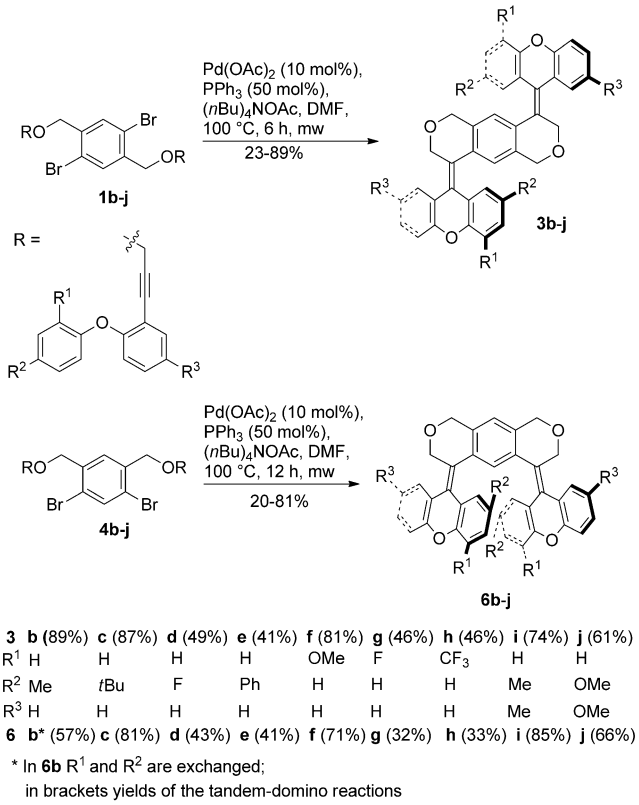


Scheme 1. Tandem-domino reaction for the synthesis of helical tetrasubstituted dialkenes **3a** and **6a**. L = ligand, mw = microwaves.



3	**b** (89%)	**c** (87%)	**d** (49%)	**e** (41%)	**f** (81%)	**g** (46%)	**h** (46%)	**i** (74%)	**j** (61%)
R^1	H	H	H	H	OMe	F	CF_3	H	H
R^2	Me	*t*Bu	F	Ph	H	H	H	Me	OMe
R^3	H	H	H	H	H	H	H	Me	OMe
6	**b*** (57%)	**c** (81%)	**d** (43%)	**e** (41%)	**f** (71%)	**g** (32%)	**h** (33%)	**i** (85%)	**j** (66%)

* In **6b** R^1 and R^2 are exchanged;
in brackets yields of the tandem-domino reactions

Scheme 2. Synthesis of helical tetrasubstituted dialkenes **3b–j** and **6b–j** using diynes **1b–j** and **4b–j** as substrates.

as base, and DMF as solvent for 12 h at 100 °C under microwave irradiation to give **6a** in an astounding yield of 97 %.

The optimized conditions were applied for the synthesis of 18 analogues with different substitution patterns as **3b–j** employing the diynes **1b–j** as well as **6b–j** employing the diynes **4b–j**; thus, diynes containing both electron-donating and -accepting groups are suitable as substrates; however, the substrates with fluoride, trifluoromethyl, and phenyl as substituents gave the lowest yields (Scheme 2).

For substrate **1h** to give **3h**, we investigated the influence of six more ligands in the Pd-catalyzed process to obtain a better yield. However, in all cases the outcome was either almost identical or inferior compared to the result obtained with PPh_3 (see the Supporting Information).

To improve the efficiency of the described processes, we even developed a six-fold tandem-domino reaction by including the two Sonogashira reactions used for the preparation of the diyne-substrates of type **1** and type **4**. Thus, **3a** could be synthesized directly from the iodoaryl ether **9a** and the dialkyne **10** in 56 % yield. The process was performed in DMF under microwave irradiation for 6 h at 100° using 10 mol % of $Pd(OAc)_2$ and PPh_3 in a ratio of 1:5 and $(nBu)_4NOAc$. It should be noted that the reaction must be carried out in the absence of copper salts, otherwise it stops after the Sonogashira reaction.

Molecules **3a** and **6a** were crystallized by slowly evaporating a solution of the compounds in chloroform in a methanol atmosphere. Both crystal structures reveal the helical chirality of the substances (Figure 1).

The synthesis of the substrates **1a–j** and **4a–j** for the tandem-domino reactions is rather simple (Scheme 3). First

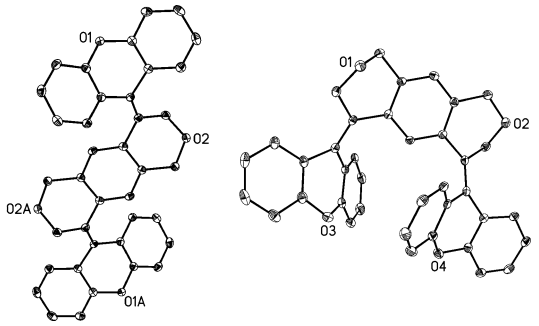
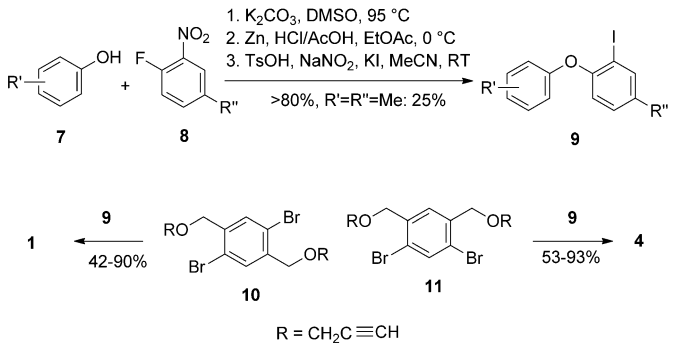


Figure 1. Crystal structures of **3a** (left) and **6a** (right).[12] The hydrogen atoms are omitted for clarity and the anisotropic displacement parameters are depicted at the 50 % probability level. Flack *x* parameter of **6a** equals 0.05 (8).[13]



7, **8**, **9**: **a**: R'=R''=H, **b**: R'=*p*-Me, R''=H, **c**: R'=*p*-*t*Bu, R''=H, **d**: R'=R'=*p*-F, R''=H, **e**: R'=*p*-Ph, R''=H, **f**: R'=*o*-OMe, R''=H, **g**: R'= *o*-F, R''=H, **h**: R'=*o*-CF_3, R''=H, **i**: R'=*p*-Me, R''=Me, **j**: R'=*p*-OMe, R''=OMe

Scheme 3. Synthesis of diynes **1** and **3** as substrates for the tandem-domino actions.

the iodoaryl ethers **9** were prepared by nucleophilic aromatic substitution of phenol **7** to fluoronitrobenzene **8** followed by reduction of the nitro group and Sandmeyer reaction. For the synthesis of the methoxy-substituted compound we used the much cheaper chloro instead of the fluoro compound. Sonogashira reaction of the iodides **9** with the dialkyne **10** led to **1** and with the dialkyne **11** to **4**. The yields range between 42 and 93%.

Photophysical investigations were performed for the compounds with an *anti* (**3a** and **3f**) and a *syn* orientation (**6a**, **6i** and **6j**) of the two helical alkene moieties, using steady-state and time-resolved spectroscopy. A comparison of absorption spectra and their changes upon irradiation are found in the Supporting Information, Figures S1 and S2, respectively. Upon irradiation, the methoxy derivative **3f** showed more visible changes in the absorption spectrum than **3a**, because the original and the switched form are spectrally more different for **3f**. Compound **6a** showed clear light-induced changes in the absorption spectrum, however with degradation (Figure 2A). Pleasingly, **6i** and **6j** also showed pronounced switching behavior, and these substituted compounds seem to be stable under irradiation (Figure 2B and C).

Femtosecond-pump–supercontinuum-probe (PSCP) spectra in the range $\lambda = 260$–700 nm were obtained for **3a**, **6a**, and **6i** using the setup described previously (cross correlation ca. 70 fs).[15] The contour plots in Figure 3 for the change in optical density (ΔOD) after excitation with a 400 nm pump pulse show that all three compounds switch upon irradiation. At early times (upper part), broad absorption appears near 600 nm and decays within ca. 1 ps (red, yellow, and greenish features represent absorption, whereas blue to violet colors show bleaching). This process is tentatively assigned to the evolution from the initially populated S_1 Franck–Condon state toward a 90° configuration by rotation around one of the alkene double bonds.[16] At the same time, new broad absorption features appear, centered around 340/580 nm (**3a**) and 360/420 nm (**6a**, **6i**). They likely arise from this perpendicular configuration. The primary photoinduced switching step therefore appears to be fast for

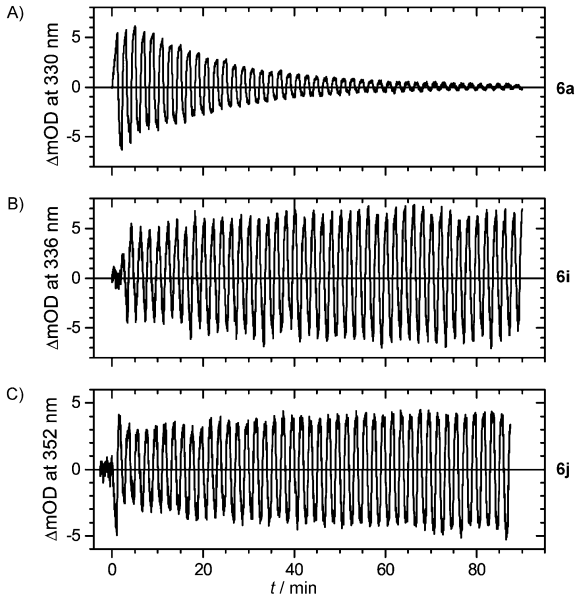


Figure 2. Change of absorption upon irradiation of A) compound **6a**, B) compound **6i**, and C) compound **6j** with alternating LED radiation with a center wavelength of $\lambda = 455$ and 528 nm.[14]

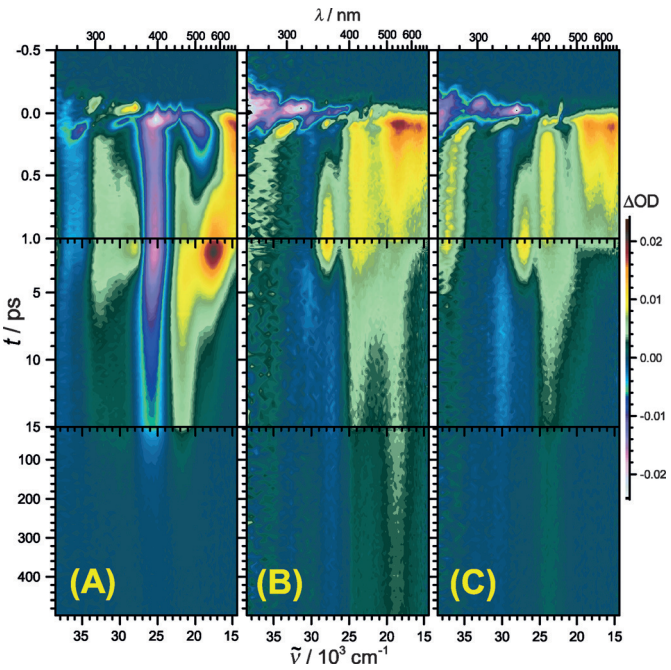


Figure 3. Contour diagram of the PSCP experiments for compounds **3a** (A), **6a** (B), and **6i** (C) in THF. The scale bar on the right represents the color code for the change in optical density, ΔOD.

all three compounds. Afterwards (middle part), the absorption feature disappears within several ps, showing that the excited molecules relax back to S_0. In the bottom panels, the long-lived absorption at ca. 520 nm for **6a** confirms the formation of a photoproduct (see also the Supporting Information, Figure S2). This is not observed for **6i**, consistent with its reversible switching behavior (Figure 2B).

Experimental Section

Synthesis of **6a**: $Pd(OAc)_2$ (1.93 mg, 86.1 μmol, 0.10 equiv), triphenylphosphane (11.3 mg, 43.1 μmol, 0.50 equiv), and nBu_4NOAc (130 mg, 431 μmol, 5.00 equiv) were added to a solution of the alkyne **4a** (61.0 mg, 86.1 μmol, 1.00 equiv) in DMF (3 mL) that had been flushed with argon. The mixture was irradiated in a microwave reactor for 12 h at 100 °C. After addition of aqueous saturated NH_4Cl solution, the mixture was extracted with dichloromethane (3 × 10 mL), the combined organic extracts were washed with brine, dried over Na_2SO_4, and the solvent was evaporated in vacuo to give an orange solid (45.7 mg, 83.6 μmol, 97 %) after column chromatography on silica gel (petroleum ether/dichloromethane = 3:1).

R_f (DCM/PE = 3/1) = 0.44. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.72 (s, 4H, 2′-H, 6′-H), 4.83 (s, 4H, 3′-H, 5′-H), 6.63 (dt, J = 7.2, 1.8 Hz, 2H, 7-H), 6.79 (s, 1H, 4′-H), 6.93 (s, 1H, 8′-H), 7.01 (dd, J = 7.2, 1.8 Hz, 2H, 8-H), 7.12–7.15 (m, 4H, 2-H, 6-H), 7.16 (dt, J = 8.4, 1.8 Hz, 7-H), 7.22 (dd, J = 7.8, 1.8 Hz, 4-H), 7.25 (dt, J = 8.4, 1.2 Hz, 3-H), 7.48 ppm (dd, J = 7.8, 1.8 Hz, 2H, 1-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 68.3 (C2′, C6′), 69.0 (C3′, C5′), 116.7 (C4), 117.4 (C5), 120.4 (C4′), 122.2 (C9), 122.4 (C7), 122.7 (C2), 124.1 (C1a), 125.6 (C8a), 126.1 (C1′), 126.6 (C1), 127.8 (C8), 127.8 (C3), 128.3 (C6), 130.2 (C1′a, C-7′a), 128.3 (C1), 136.2 (C3′a, C4′a), 153.7 (C5a), 154.5 ppm (C4a). UV ($CHCl_3$): λ_{max} (log ε) = 284 nm (4.2136), 329 (4.3493). IR: $\tilde{\nu}$ = 3062, 2953, 2834, 1594, 1471, 1446, 1250, 1119, 1096, 859, 771, 749 cm^{-1}. MS (ESI): m/z = 547.2 $[M+H]^+$. HMRS for $C_{38}H_{26}O_4$ calcd: 547.1904, found: 547.1894 $[M+H]^+$ (ESI-HRMS). $C_{38}H_{26}O_4$ (546.62).

Keywords: C–H activation · domino reactions · helical structures · molecular devices · palladium

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[12] CCDC 1049106 (**3a**) and 1049107 (**6a**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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[14] Optical switching experiments: Compounds **6a**, **6i**, and **6j** were dissolved in THF and circulated by a micropump through first a photoreaction flow cell and then an absorption cuvette (path length 10 mm), which was placed in a Varian Cary 5000 spectrometer. The molecules in the photoreaction cell were subjected to alternating radiation of two LED stacks (center wavelength 455 and 528 nm, respectively) which were switched back and forth every 60 s. The change in absorption was recorded at fixed wavelengths, and subsequently the baseline drift for approaching the photostationary state was subtracted. Results are shown in Figure 2. The switching amplitude of **6a** decreases, suggesting the formation of a stable photoproduct which does not switch any longer. On the other hand, **6i** and **6j** show stable switching behavior and do not exhibit any sign of photoproduct formation. Presumably, the unwanted side reaction is blocked as a result of steric hindrance by the additional methyl (**6i**) and methoxy (**6j**) substituents, respectively.

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