# Synthesis, stereochemistry, and photochemical and thermal behaviour of bis-*tert*-butyl substituted overcrowded alkenes†

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In order to study the structural limits in the design of molecular motors, a *tert*-butyl substituted analogue was prepared. The unexpected photochemical and thermal isomerisation processes and the stereochemistry of new overcrowded alkene **5** are described. The bis *tert*-butyl substituted alkenes were synthesised in a five-step sequence with an overall yield of 7.5%. Structural assignments of the isomers based on experimental data were supported by calculations of all four isomers of the alkene. X-Ray crystal analysis showed a strongly twisted alkene (torsion angle 39°) for a less stable photochemically generated *cis*-isomer.

## Introduction

Fundamental knowledge of organic compounds where structural parameters have been pushed to the limit (*e.g.* steric crowding in alkenes and deviation from arene planarity) have led to a plethora of remarkable molecules.[1,2] The challenge to prepare such compounds has frequently been a major incentive to develop new synthetic procedures. Most of these compounds have, however, found little application in functional devices. The overcrowded biphenanthrylidenes **1–3** (Fig. 1),[3] whose helical structures resemble in some respect the structure of helicenes, are not only interesting molecules from a fundamental point of view, but might find application in nanotechnological devices.[4]

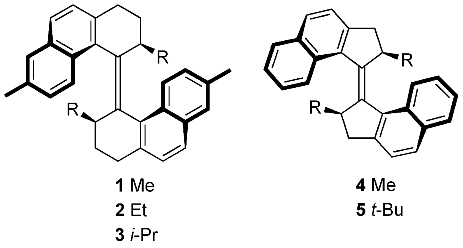

**Fig. 1** Overcrowded alkenes **1–5**; compounds **1–4** function as unidirectional light-driven molecular motors.

The motor molecules **1–4** are able to perform, in a four-step sequence, a 360° unidirectional rotation around the central double bond (the rotary axis) and function as light-driven molecular motors.[5] The whole rotation process is fueled by light energy, which induces two photochemical *cis–trans* isomerisations of the double bond. Each photochemical isomerisation is followed by a thermally driven helix inversion. During this thermal process, a change in the orientation of the R-substituents takes place from the energetically unfavorable (pseudo-)equatorial to the energetically favorable (pseudo-)axial orientation. The thermal process is irreversible and it accounts for the unidirectionality of the entire rotary process. Since the size of the R-substituents is of particular importance for the motor function, ethyl and isopropyl substituted molecular motors **2** and **3** were synthesised.[5] Interestingly, replacing the methyl substituents in **1** by the larger isopropyl substituents in **3** revealed that the thermal isomerisations of the motor molecules proceed in two consecutive steps. It was demonstrated that the thermal helix inversion of a molecule with (*M*,*M*)-helix to a molecule with a (*P*,*P*)-helix proceeds *via* an intermediate with a (*P*,*M*) helical structure.[5]

A major disadvantage of motor **1** is the relatively low rate of the thermal helix inversion and therefore slow overall rotation. We have designed and synthesised motor molecule **4**, in which the two six-membered rings as in **1** have been replaced by two five-membered rings. An important feature of motor molecule **4** is its enhanced speed of rotation, due to the enhanced rate of the thermal helix inversion. This is probably a direct consequence of the reduced steric hindrance around the central double bond. This is indirectly reflected in the synthesis of the motor molecules **1–4** for which in the final, and most difficult step a McMurry reaction is used to form the sterically overcrowded double bond. Whereas the synthesis of **1**, **2** and especially **3** is quite troublesome, the last step in the synthesis of motor **4** is readily performed and proceeds in good yields.

Independently, overcrowded alkene **4** has been studied in the group of Harada.[6] In their detailed studies, they have shown that the original assignment of the absolute configuration of **4** had to be revised. We became interested in the thermal and photochemical properties of overcrowded alkene **5**, which is expected to show severe steric hindrance compared to its analogue **4**. In **5** the two methyl substituents are to be replaced by two bulky *tert*-butyl substituents. It was anticipated, that like in the case of **1** and **3**, the increase of steric bulk would allow more detailed studies of substituent effects on the photochemical and thermal isomerisation processes for the molecular motors containing two five-membered rings.

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† Electronic supplementary information (ESI) available: Details of calculations. Table S1: Calculated structures for the four isomers of **4** and the experimental structural data of stable *cis*-**4** and stable *trans*-**4**. Table S2: Calculated structures for all four isomers of **5** and the experimental data for both *cis*-isomers of **5** from X-ray crystallography. See DOI: 10.1039/b611070c

## Synthesis

The preparation of alkene **5** (Scheme 1) is straight-forward and follows the synthetic scheme that has originally been applied to **4**. A feature is, however, that due to the increasing steric bulk of the *tert*-butyl group, these reactions are much slower and require extended reaction times. The synthesis starts with the commercially available acid **6**, which was converted to ester **7** in good yield by reaction with methyl iodide in DMF in the presence of base. Deprotonation of the ester **7** using LDA in THF at low temperature and subsequent alkylation with **8** gave the desired ester **9** in moderate yield. This ester **9** could be cleaved only using harsh conditions, but acid **10** was eventually obtained in good yield after refluxing for six days in a mixture of ethanol and water containing KOH. Acid **10** was converted to the ketone **11** using standard Friedel–Crafts conditions, employing $SOCl_2$ and $AlCl_3$. Preliminary attempts to couple this ketone using the McMurry reaction with $TiCl_4$ and zinc powder resulted in the recovery of the starting material. However, using prolonged reaction times of nearly two weeks, the desired alkene **5** was obtained as a mixture of (2*S**,2′*S**)-(*P**,*P**)-*cis*- and (2*S**,2′*S**)-(*P**,*P**)-*trans*-isomers in an approximate 5 : 2 ratio and in a combined yield of 19%.[7] Analysis of the crude reaction mixture showed that apart from the mixture of *cis*-**5** and *trans*-**5**, still a part of the starting ketone **11** remained present, indicating that even longer reaction times might yield more of the product. Surprisingly, in this McMurry reaction the formation of the usual side-products was not observed.[8] Eventually, the *cis*-**5** isomer was obtained pure by multiple precipitations and recrystallisations from heptane. Unfortunately, the *trans*-**5** isomer could not be obtained in pure form in this way (*vide infra*) and could only be obtained pure after photochemical isomerisation of *cis*-**5**. The structures of both isomers were assigned by comparison of the $^1$H NMR spectra of **5** with those of the corresponding *cis* and *trans* isomers of the methyl substituted five-membered ring molecular motor **4**. Informative in this respect are the absorptions of $H_8$ and $H_9$ for the *cis*-isomer of **5** at high field ($\delta$ 6.3 ppm) and the absorption of $H_9$ for *trans*-**5** at low field ($\delta$ 8.7 ppm) (for numbering see Fig. 2(d)). Summarizing, the alkene **5** was, considering the steric bulk introduced into the final molecule, efficiently synthesised in a five-step sequence in an overall yield of 7.5%.

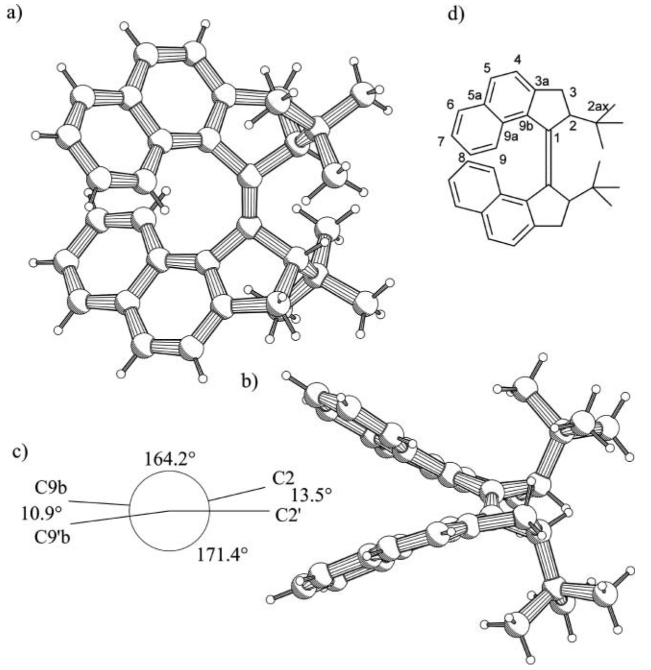
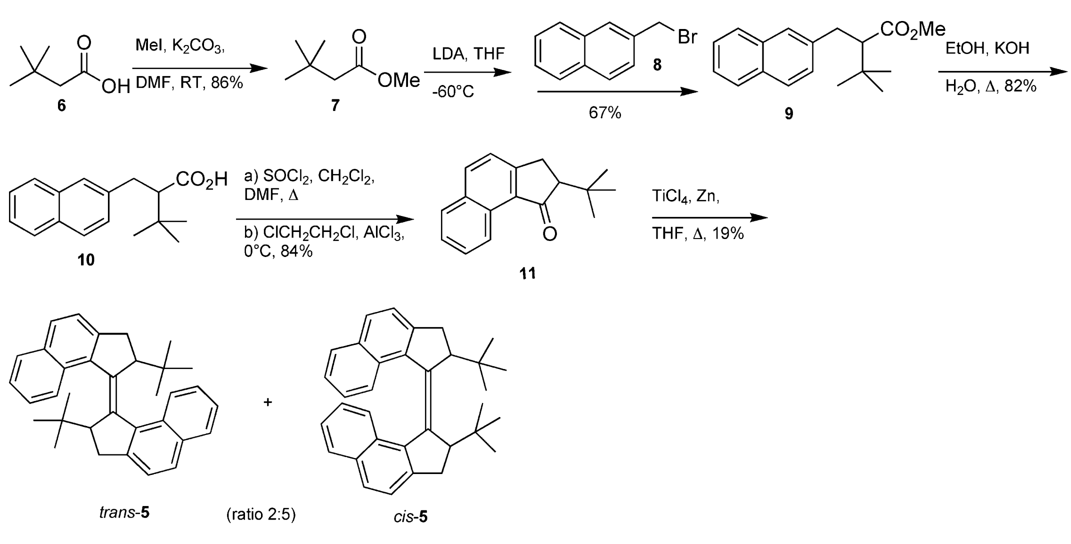


**Fig. 2** PLUTO drawings of racemic (2*S**,2′*S**)-(*P**,*P**)-*cis*-(±)-2,2′-di-*tert*-butyl-2,2′,3,3′-tetrahydro-1,1′-bicyclopenta[*a*]naphthalenylidene (**5**) viewed perpendicular (a) to the central double bond and along (b) the central double bond; Newman projection of the configuration around the central double bond (viewed along the axis $C_1$–$C_{1'}$) (c) as well as the numbering scheme adopted for the molecule (d) are depicted.

Further evidence for the structural assignment of *cis*-**5** was obtained by X-ray analysis. Sharp, colorless platelets of *cis*-**5** suitable for X-ray crystallographic analysis were obtained by slow recrystallisation from heptane (Fig. 2).[9]

The overall molecular shape of *tert*-butyl substituted *cis*-**5** shows only minor differences compared to the methyl substituted analogue *cis*-**4**. The structure of *cis*-**5**, which is $C_2$-symmetric in solution as could be seen from the $^1$H and $^{13}$C NMR spectra,



**Scheme 1** The synthesis of overcrowded alkene **5**.

deviates slightly from this preferred geometry in the solid state due to crystal packing effects. The helical shape and the (pseudo-)axial orientation of the *tert*-butyl substituents are the most noteworthy structural features. The naphthalene moiety and the *tert*-butyl substituent in each half of the molecule in *cis*-**5** are found to be oriented in the same direction. The length of the central double bond was found to deviate only slightly from literature values: 1.353 Å.[10] The geometry of *cis*-**5** around the central double bond (see also the Newman projection in Fig. 2) is similar to that of *cis*-**4**. The bond angles around $C_1$ and $C_{1'}$ are: $C_2$–$C_1$–$C_{9b}$ = 104.1°, $C_2$–$C_1$–$C_{1'}$ = 124.2° and $C_{9b}$–$C_1$–$C_{1'}$ = 130.9° (average total angle around $C_1$ and $C_{1'}$ = 359.8°). The values for the torsion angles around the double bond are: $C_2$–$C_1$–$C_{1'}$–$C_{2'}$ = −13.5°, $C_{9b}$–$C_1$–$C_{1'}$–$C_{9'b}$ = 10.9° and $C_2$–$C_1$–$C_{1'}$–$C_{9'b}$ = 178.7° (average). These values are averages of values in the two parts of the molecule since the structure is pseudo-$C_2$-symmetric.

As can be seen from the Newman projection, the deviation from the plane of the central double bond is considerable and is approximately 10° to both sides. The two five-membered rings in the molecule are only slightly twisted and the atoms $C_1$, $C_2$ and $C_3$ only slightly deviate from the least-squares plane through $C_1$, $C_2$, $C_3$, $C_{3a}$ and $C_{9b}$.

## Photochemical and thermal experiments

In order to investigate whether this molecule functions as a motor and to examine the photochemical behavior of **5**, enantiomerically pure material was needed for CD measurements. The stable *cis*-**5** could be resolved by chiral preparative HPLC using a Chiralcel OD column as the stationary phase and a mixture of heptane–isopropyl alcohol = 99.75 : 0.25 as the eluent. In order to determine the absolute configuration of the two enantiomers, the spectra of the first eluted fraction of *cis*-**5** and the spectrum of (2*S*,2′*S*)-(*M*,*M*)-*cis*-**4** obtained by Harada *et al.* were compared.[6] As can be seen from Fig. 3, the UV-Vis and CD spectra are similar in shape.

Noteworthy is the large difference in intensity of the absorption in the CD spectrum at 233.6 nm, which has nearly doubled in magnitude (and with opposite sign) for **5** compared to **4**. On the basis of this comparison, the absolute configuration of the enantiomer in the first eluted fraction of the *tert*-butyl substituted compound was assigned (2*S*,2′*S*)-(*P*,*P*)-*cis*-**5**.

Irradiation of a solution of (2*S*,2′*S*)-(*P*,*P*)-*cis*-**5** in *n*-hexane at low temperature ($\lambda \geq 280$ nm, $T = -25$ °C) gave complete conversion to a new isomer of **5**, as was determined by HPLC and mass spectrometry. The solution of (2*S*,2′*S*)-(*P*,*P*)-*cis*-**5**, which was colorless, turned rapidly orange upon irradiation and an absorption band appeared as high as 480 nm in the UV-Vis spectrum. Coloration of the sample is observed in all cases for unstable forms of the motors molecules **1**–**4**, but never as intense and as red-shifted as for this particular isomer of **5**. The UV-Vis and CD spectra of this new isomer are depicted in Fig. 4.

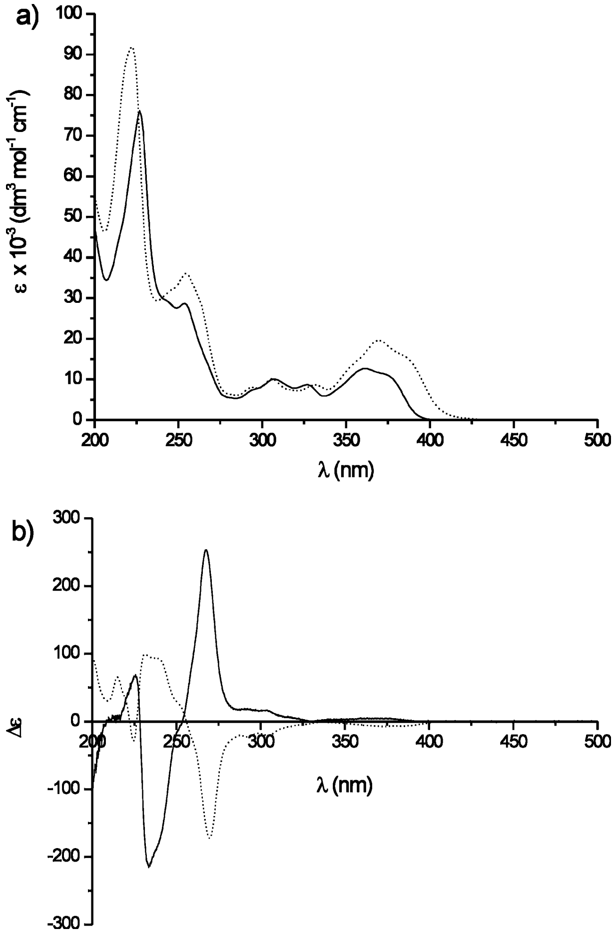


**Fig. 3** UV-Vis (a) and CD spectra (b) of (2*S*,2′*S*)-(*P*,*P*)-*cis*-**5** (solid line) and (2*S*,2′*S*)-(*M*,*M*)-*cis*-**4** (dotted line) in *n*-hexane.

The CD absorptions of the newly formed isomer are not as intense as those of stable (2*S*,2′*S*)-(*P*,*P*)-*cis*-**5**. The most intense absorption is found at 223.0 nm ($\Delta\varepsilon = -157.7$), other signals at longer wavelengths are significantly less intense. Based on photochemical experiments with **1**–**4**, it was anticipated that upon irradiation of (2*S*,2′*S*)-(*P*,*P*)-*cis*-**5** photoisomerisation at the central double bond had taken place to form the unstable (2*S*,2′*S*)-(*M*,*M*)-*trans*-**5**. However, comparison of the CD spectrum of the new isomer of **5** with that of the unstable (2*S*,2′*S*)-(*P*,*P*)-*trans*-**4** or even unstable (2*S*,2′*S*)-(*P*,*P*)-*cis*-**4**, did not give decisive evidence for the formation of either unstable isomer of alkene **5**. Upon heating the sample in *n*-hexane at 60 °C, no decoloration was observed, pointing out the relative stability of this newly formed isomer. Only when a sample was dissolved in dodecane, allowing heating at elevated temperatures (*e.g.* $T$ = 90 °C), decoloration of the sample was observed, leading to the formation of (2*S*,2′*S*)-(*P*,*P*)-*trans*-**5**, as was confirmed by HPLC, UV-Vis and CD spectroscopy (see Fig. 4). The UV-Vis spectrum shows clearly the two absorption maxima at 350 and 360 nm, which are characteristic for (2*S*,2′*S*)-(*P*,*P*)-*trans*-**5**. This photochemical isomerisation followed by a thermal isomerisation of the molecule proved to be the only way to obtain pure (2*S**,2′*S**)-(*P**,*P**)-*trans*-**5** because this compound could not obtained in pure form from the reaction mixture. Also in the case of (2*S*,2′*S*)-(*P*,*P*)-*trans*-**5**, the CD spectrum does not have the intense Cotton effects that were found for (2*S*,2′*S*)-(*M*,*M*)-*trans*-**4**. The only obvious similarity between the two CD spectra is the absorption in the CD at 259.2 nm ($\Delta\varepsilon$ = +158.7) for stable (2*S*,2′*S*)-(*P*,*P*)-*trans*-**5** and at 258.0 nm ($\Delta\varepsilon$ = −236.5) for the stable *trans*-**4** isomer. The other Cotton effects in the CD spectrum are surprisingly small for such a helical shaped molecule.

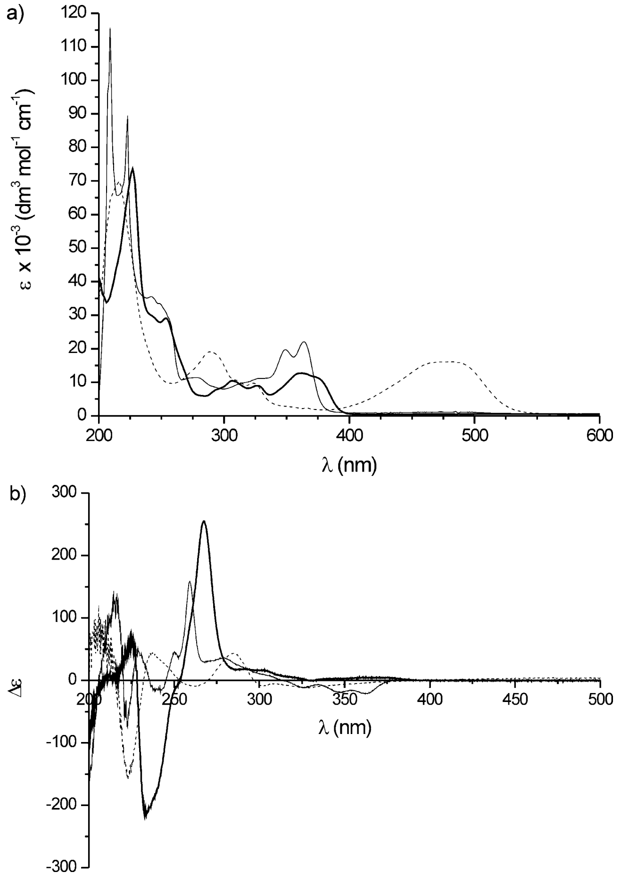
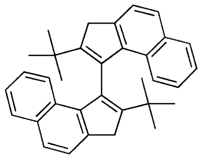


**Fig. 4** UV-Vis (*n*-hexane) (a) and CD (*n*-hexane) (b) spectra of the isomers of *tert*-butyl substituted olefin **5**. Stable (2*S*,2′*S*)-(*P*,*P*)-*cis*-**5** (thick solid line), unknown isomer of **5** (dashed line) and stable (2*S*,2′*S*)-(*P*,*P*)-*trans* (solid line).

In order to quantify the height of the activation barrier for the conversion of the new isomer of **5** into the stable (2*S*,2′*S*)-(*P*,*P*)-*trans*-**5** isomer, a sample of (2*S*,2′*S*)-(*P*,*P*)-*cis*-**5** in dodecane was irradiated ($\lambda \geq 280$ nm, $T = -25$ °C). The sample was then heated at various temperatures (70, 80, 90, 100 °C) while the intensity of the CD-signal at 230 nm was monitored, indicating the decay of the newly formed isomer of **5**. The kinetic data revealed that a unimolecular process took place going from the new isomer of **5** to the stable (2*S*,2′*S*)-(*P*,*P*)-*trans*-**5**. With the aid of an Eyring plot, these data were used to calculate both the Gibbs energy ($\Delta G_0{}^{\ddagger} = 105 \pm 4$ kJ mol$^{-1}$), the enthalpy ($\Delta H_0{}^{\ddagger} = 76 \pm 4$ kJ mol$^{-1}$) and the entropy of activation ($\Delta S_0{}^{\ddagger} = -100 \pm 10$ J K$^{-1}$ mol$^{-1}$) and the half-life of the thermal helix inversion at room temperature ($t_{1/2} = 193$ h, 293.15 K).

Unfortunately, the isomers of **5** are not as robust as previously examined molecular motors. Upon prolonged (>24 h) irradiation of a sample with a low concentration ($\sim 1 \times 10^{-5}$ M) at $\lambda \geq 280$ nm photo-degradation took place to multiple products which precipitated from the solution.

As indicated above, the actual structure of the new isomer could not be assigned unequivocally by comparison with the UV-Vis and CD spectroscopic data of previously prepared switches or motor molecules. Therefore, irradiation experiments ($\lambda \geq 280$ nm, $T = 20$ °C) were performed with a mixture of stable *trans*-**5** and stable *cis*-**5** in toluene-d$_8$ and benzene-d$_6$ in order to generate quantitatively the unknown isomer of **5**. The assignment of the geometry of the unknown isomer of **5** on basis of $^1$H NMR spectroscopy was difficult. The arene protons absorbing at relatively high field, $\delta$ 6.4 and 6.8 ppm, are normally indicative for molecules with a *cis*-geometry. These shifts to higher field are due to the ring current anisotropy of the neighboring naphthalene moiety. At the same time, no absorption was observed at low field at approximately $\delta$ 8.0 ppm which would indicate a *trans*-geometry. However, in the NOE spectrum, a small interaction was observed between the protons of the *tert*-butyl and the protons at C$_9$ of the naphthalene ring, which is usually observed for *trans*-isomers, but not for *cis*-isomers. Interestingly, while following the photochemical reaction by $^1$H NMR spectroscopy, first the stable *trans*-**5** is converted completely to the unknown isomer of **5**, followed by a slower, complete conversion of *cis*-**5** to the unknown isomer of **5**. After prolonged irradiation of a sample with an intermediate concentration of **5** ($\sim 1 \times 10^{-3}$ M), a number of decomposition products appeared in the spectrum. One side product **12** could be isolated in small quantities from an irradiated sample of *cis*-**5** and *trans*-**5** and characterised (Fig. 5). So far, these or similar side-products, have not been observed for either six-membered molecular motors **1–3** or for the five-membered molecular motor **4**.



**12**

**Fig. 5** Photodegradation product **12** isolated after irradiation of a mixture of *cis*-**5** and *trans*-**5**.

Heating of the unknown isomer of **5** at 100 °C in a toluene-d$_8$ solution showed a rapid conversion to the stable *trans*-**5**, followed by the very slow (days in boiling toluene-d$_8$) thermal conversion of stable *trans*-**5** to the stable *cis*-**5**. This is another indication, apart from the preferred formation of the *cis*-**5** over *trans*-**5** in the synthesis, that *cis*-**5** is thermodynamically more stable than *trans*-**5**. Since still no conclusive evidence could be presented to unequivocally establish the structure of the new isomer, an X-ray crystallographic analysis was performed. The unknown isomer of **5** was generated by irradiation ($\lambda \geq 280$ nm, $T = 20$ °C) of a solution of stable (2*S**,2′*S**)-(*P**,*P**)-*cis*-**5** and stable (2*S**,2′*S**)-(*P**,*P**)-*trans*-**5** in toluene-d$_8$. Due to the small amounts obtained of the unknown isomer of **5**, crystallisation proved to be difficult. A small orange crystal suitable for X-ray crystallographic analysis could be obtained by slow diffusion of methanol in an *n*-hexane solution of **5**.[11] Surprisingly, the unknown isomer of **5** obtained after irradiation proved to be the (2*S**,2′*S**)-(*M**,*M**)-*cis*-**5**, as can be seen from Fig. 6.

The helical structure of (2*S**,2′*S**)-(*M**,*M**)-*cis*-**5** is inverted compared to stable (2*S**,2′*S**)-(*P**,*P**)-*cis*-**5**. Although the X-ray crystal structure of the unstable *cis*-**5** suggests that the compound is $C_2$-symmetric in the solid state, it is slightly distorted from its preferred $C_2$-symmetric geometry in solution. A remarkable feature of the molecule is the twisted nature of the compound. Not only is the central double bond severely twisted, but also the two

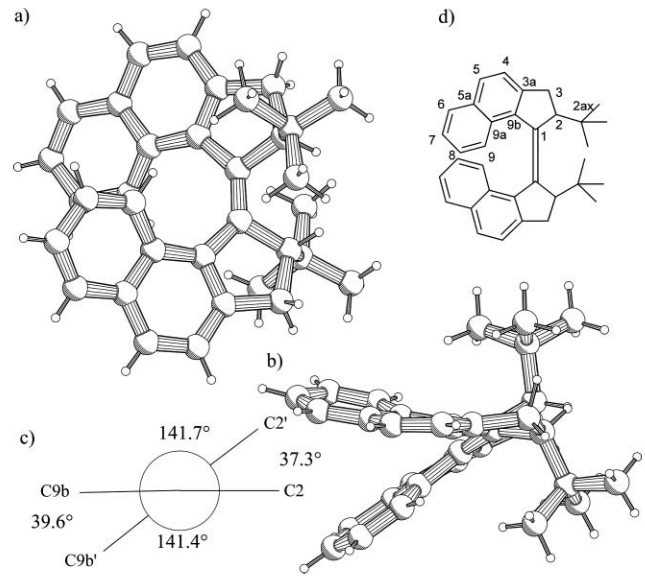


**Fig. 6** PLUTO drawings of racemic (2*S**,2′*S**)-(*M**,*M**)-*cis*-(±)-2,2′-di-*tert*-butyl-2,2′,3,3′-tetrahydro-1,1′-bicyclopenta[*a*]naphthalenylidene (**5**) viewed perpendicularly (a) and along (b) the central double bond; Newman projection viewing along the central double bond $C_1$–$C_{1'}$ (c) and the adopted numbering scheme (d).

naphthalene moieties are deformed. This all in order to keep the *tert*-butyl substituents in an axial position (torsion angle $C_{1'}$–$C_1$–$C_2$–$C_{2ax}$ (average, 73.7°)). The central double bond is significantly longer, 1.379 Å, than that of, for example, stable (2*R**,2′*R**)-(*P**,*P**)-*cis*-**4** (1.359 Å, average) and (2*S**,2′*S**)-(*P**,*P**)-*cis*-**5** (1.353 Å). The angles around the carbon atoms $C_1$ and $C_{1'}$ of the central double bond are characterised as follows: $C_2$–$C_1$–$C_{9b}$ (107.02°), $C_2$–$C_1$–$C_{1'}$ (120.87°), $C_{9b}$–$C_1$–$C_{1'}$ (132.11°), $C_{2'}$–$C_{1'}$–$C_{9'b}$ (107.03°), $C_{2'}$–$C_{1'}$–$C_1$ (119.86°) and $C_{9'b}$–$C_{1'}$–$C_1$ (133.10) giving total angles around $C_1$ of 360.0° and $C_{1'}$ of 360.0°. From the torsion angles $C_2$–$C_1$–$C_{1'}$–$C_2 = -37.3°$, $C_{9b}$–$C_1$–$C_{1'}$–$C_{9'b} = -39.6°$ and $C_2$–$C_1$–$C_{1'}$–$C_{9'b}$ = 141.58° (average), it can be seen that the central double bond is severely twisted. This is especially obvious from the Newman projection in Fig. 6 and by comparison with the corresponding torsion angles of stable (2*S**,2′*S**)-(*P**,*P**)-*cis*-**5** being: $C_2$–$C_1$–$C_{1'}$–$C_2$ = 13.5°, $C_{9b}$–$C_1$–$C_{1'}$–$C_{9'b}$ = 10.9° and $C_2$–$C_1$–$C_{1'}$–$C_{9'b}$ = 178.7° (average), respectively. The torsion angle $C_{9a}$–$C_{9b}$–$C_1$–$C_{1'}$ is in the unstable (2*S**,2′*S**)-(*M**,*M**)-*cis*-**5** reduced to only 6.4° (average). In the stable *cis*-isomers, this torsion angle normally nicely reflects the angle between both naphthalene chromophores. In the present case, however, the central double bond is twisted to such an extent that it no longer reflects this angle (42.0°) correctly. Also the naphthalene moieties themselves are bent. Whereas in each half of the molecule one aromatic ring is relatively flat ($C_{5a}$–$C_6$–$C_7$–$C_8$–$C_9$–$C_{9a}$ and $C_{5'a}$–$C_{6'}$–$C_{7'}$–$C_{8'}$–$C_{9'}$–$C_{9'a}$) the remaining atoms in the naphthalene moiety are bent away to avoid steric hindrance. The deviations from the least-square planes through the aromatic rings are quite large: $C_{3a}$ (−0.40 Å), $C_4$ (0.51 Å), $C_5$ (−0.26 Å), $C_{9b}$ (0.02 Å), $C_{3a}$ (−0.19 Å), $C_{4'}$ (0.28 Å), $C_{5'}$ (−0.15 Å) and $C_{9'b}$ (0.10 Å). The five-membered rings are relatively flat and the deviations for $C_1$, $C_2$ and $C_3$ from the least-square plane through $C_1$–$C_2$–$C_3$–$C_{3a}$–$C_{9b}$ are not larger than 0.11 Å. Compared to several examples of torsional distorted alkenes described in the literature, the unstable (2*S**,2′*S**)-(*M**,*M**)-*cis*-**5** contains one of the most twisted double bonds. The only alkenes reported which contained a double bond that is not influenced by push–pull substituents with a larger twist are the alkenes **13**,[12] **14**[13] and its derivatives, **15**[14] and **16**[14] (Fig. 7)

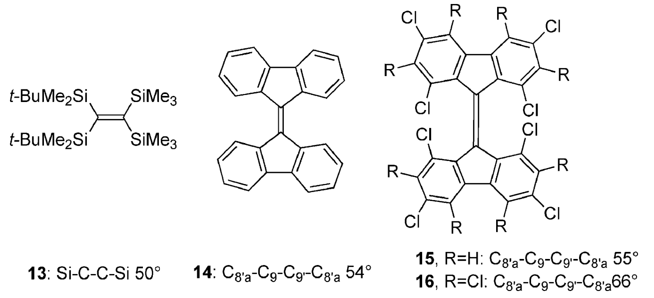
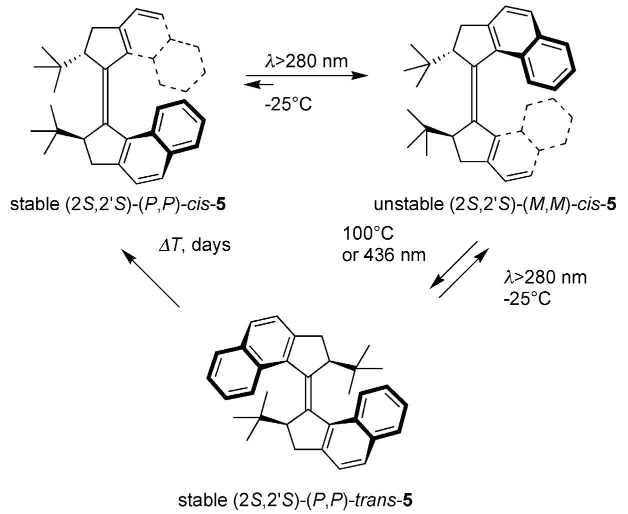


**Fig. 7** Alkenes **13** and **14–16** with a larger twist of the central double bond than that found in (2*S**,2′*S**)-(*M**,*M**)-*cis*-**5**.

### Three-stage isomerisation cycle

Summarizing the observations above, the following scheme can be drawn for the *tert*-butyl substituted alkene **5** (Scheme 2). Photoirradiation of either stable (2*S**,2′*S**)-(*P**,*P**)-*trans*-**5** or stable (2*S**,2′*S**)-(*P**,*P**)-*cis*-**5** at $\lambda \geq 280$ nm leads to the quantitative formation of the unstable (2*S**,2′*S**)-(*M**,*M**)-*cis*-**5**. Heating at elevated temperatures of unstable (2*S**,2′*S**)-(*M**,*M**)-*cis*-**5** gives the stable (2*S**,2′*S**)-(*P**,*P**)-*trans*-**5**. The same reaction can also be performed by irradiation of the unstable (2*S**,2′*S**)-(*M**,*M**)-*cis*-**5** with light ($\lambda = 436$ nm). Further heating of stable (2*S**,2′*S**)-(*P**,*P**)-*trans*-**5** completes the cycle and reverts the system *via* a slow thermal isomerisation to the starting point as the stable (2*S**,2′*S**)-(*P**,*P**)-*cis*-**5** is regenerated. It is remarkable that, in contrast to **4**, no unstable *trans* isomer of **5** could be detected.



**Scheme 2** Photochemical and thermal isomerisations of *tert*-butyl substituted alkene **5**.

## Calculations

In order to gain insight into the structure and the relative stabilities of the isomers of alkene **5**, their structures were calculated. The availability of simple, reliable methodology for the calculation of the structural parameters is especially of importance for isomers for which no X-ray analysis can be performed. Methodology previously used for calculation of the structures of the first generation molecular motors such as **1**, containing two six-membered rings, required long calculation times.[15] The presence of two five-membered rings in molecules **4** and **5**, however, means that these molecules are much less flexible and the number of conformational possibilities is therefore limited to those with an anticipated pseudo-axial or pseudo-equatorial orientation of the substituents at the stereogenic centers. It was felt that the structure of these alkenes strongly depends on the steric interactions between the two halves of molecule and therefore on the value of dihedral angle $C_2$–$C_1$–$C_{1'}$–$C_{2'}$. Due to its structural similarity and availability of both X-ray and CD data, methyl substituted motor molecule **4** was chosen as a comparison to test the calculation methodology.

At first the relation between the energy of molecule and its structure was estimated at the AM1 semi-empirical level and then optimised at the b3lyp/6-31g(d)//b3lyp/3-21g(d) level.[16] The comparison of the calculated structures with experimental X-ray data showed excellent agreement and shows that this semi-empirical-DFT methodology can be used for the prediction of structurally related molecules.[17]

As was assumed on basis of the outcome of the synthesis of **4**, the isomer with the lowest energy was stable *cis*-**4** followed by stable *trans*-**4** which was found to be 11.0 kJ mol$^{-1}$ higher in energy (see Table 1). The unstable isomers *trans*-**4** and *cis*-**4** were respectively 20.2 and 26.5 kJ mol$^{-1}$ higher in energy than the stable-*cis*-**4**. These values only reflect the relative energies of the different isomers of **4** and not the rate of the thermal helix inversion that depends on the activation energy.

The conformations of lowest-energy of the isomers of **4** were then used as starting points for the computation of the accessible isomers of **5**. First, the methyl groups at $C_2$ and $C_{2'}$ in the stable forms of **4** were replaced by *tert*-butyl substituents and full structure optimisations were performed for all compounds at the AM1 semi-empirical level, followed by systematic conformational search at the same level for each previously optimised structure according to the procedure described for **4**.

**Table 1** Results of the calculated structures the four isomers of **4** and **5**

| | | $\Delta E$/kJ mol$^{-1}$ |
|---|---|---|
| Stable *cis* | Me-**4** | 0.0 |
| | *t*Bu-**5** | 0.0 |
| Unstable *cis* | Me-**4** | +26.5 |
| | *t*Bu-**5** | +57.5 |
| Stable *trans* | Me-**4** | +11.0 |
| | *t*Bu-**5** | +42.0 |
| Unstable *trans* | Me-**4** | +20.2 |
| | *t*Bu-**5** | +89.7 |

Similar to **4**, *cis*-**5** with pseudo-axial *tert*-butyl substituents was of the lowest energy followed by the *trans*-**5** isomer with axial *tert*-butyl substituents which is 42.0 kJ mol$^{-1}$ higher in energy (see Table 1 and Fig. 8).[17] The unstable *cis*-**5** isomer, due to the steric crowding also with pseudo-axial *tert*-butyl substituents, was 15.5 kJ mol$^{-1}$ higher in energy than the stable *trans*-**5** isomer with pseudo-axial substituents (57.5 kJ mol$^{-1}$ compared to axial *cis*-**5**). The highest energy conformer was the unstable *trans*-**5**, which was no less than 89.7 kJ mol$^{-1}$ higher in energy than axial substituted *cis*-**5**. The differences in relative energies between respective conformers of **4** and **5** are of steric origin. Bulky substituents such as the *tert*-butyl groups cause distortions around the central double bond and also severely distort the naphthalene moieties, as can be seen from the X-ray and calculations of the unstable isomers. Similarly, the bulky substituents do have a profound impact on the barriers of isomerisation, as the unstable *cis* isomer of **4** is thermally unstable, the unstable *cis*-**5** can be isolated and characterized due the steric hindrance induced by the same *tert*-butyl substituents.

## Discussion and conclusion

The experimental observations presented above for alkene **5** are different from all molecular motors described so far. Contrary to the usual rotary behavior of the overcrowded alkenes, no evidence for the formation of the unstable *trans*-**5** was found. The existence of the three other forms, stable and unstable *cis*-**5** and stable *trans*-**5** could be confirmed experimentally. Two important differences in the behavior of bis-*tert*-butyl substituted alkene **5** compared to, for example, the related bis-methyl substituted alkene **4** have to be

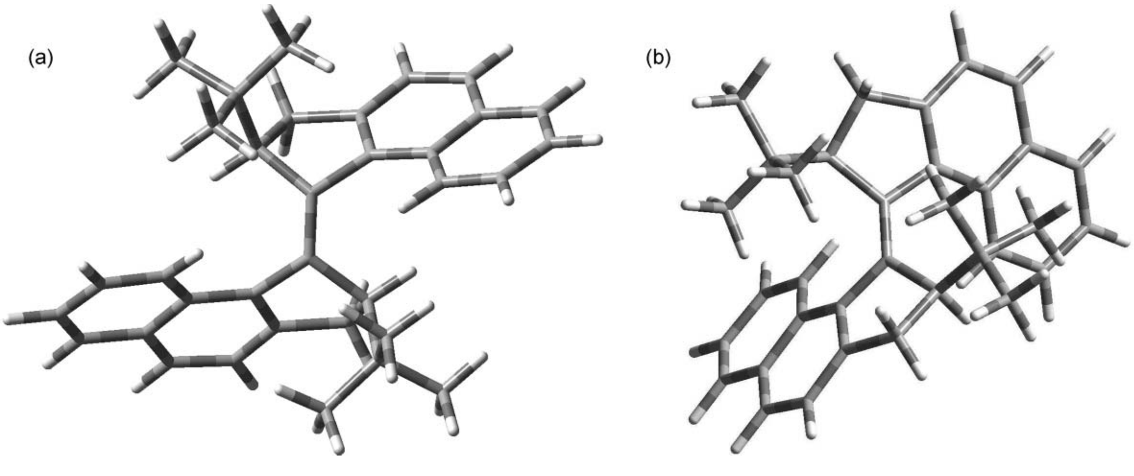


**Fig. 8** Calculated structures of the stable (a) and unstable (b) *trans* isomers of **5**.

noted. The first difference is that irradiation of a stable *cis*-isomer would normally lead to the formation of an unstable *trans*-isomer. In case of **5**, irradiation of the stable *cis*-**5** gives the unstable *cis*-**5** isomer. Apparently, upon relaxation from the excited state, there is a preference for the pathway leading to formation of unstable *cis*-**5**. From stable *cis*-**5** it is difficult to form the unstable *trans*-**5** because of the presence of two very bulky *tert*-butyl substituents which have to pass along each other. It is much easier for the two naphthalene moieties to flip along each other. Therefore, refolding in the excited state followed by relaxation to the ground-state takes place along a pathway that eventually leads to the unstable *cis*-**5**. Although experimentally unstable *trans*-**5** was not observed, calculations indicate that this isomer is found at an energy minimum, but that it is significantly higher in energy than the other three isomers.

A second difference is that heating of an unstable *cis*- or *trans*-isomer normally would lead to the stable *cis*- or *trans*-isomeric counterparts. The thermal conversion of unstable *cis*-**5** to stable *trans*-**5** observed here has no precedent. This interconversion takes place at elevated temperatures at moderate speed.

Other characteristics of alkene **5** have precedents. For example, overcrowded alkene **1** is able to switch selectively between the stable *cis*-**1** and the unstable *trans*-**1**.[18] The present overcrowded alkene **5** could in principle also function as such a perfect chiroptical switch with full conversion in either way and simple read-out. A negative aspect is the production of various side-products upon prolonged irradiation of which **12** could be isolated and characterised. These side-products were, however, only obtained after prolonged irradiation times (hours) with polychromatic light ($\lambda \geq 280$ nm). Upon irradiation of stable *trans*-**5** with light ($\lambda \geq 280$ nm) the system completely switches to the unstable *cis*-**5**. Reversal of the process is accomplished by irradiation with blue light ($\lambda = 436$ nm) (Scheme 2). Probably irradiation of *trans*-**5** leads to the same exited state as is reached upon irradiation of stable *cis*-**5**. Finally, the stable *trans*-**5** is thermally converted to the stable *cis*-**5**.

The overcrowded alkene **5** could in principle also function as a molecular motor. The unidirectional rotation can, however, not be proven unequivocally. The problem is that during the thermal conversion of stable *trans*-**5** to stable *cis*-**5**, the two halves of the molecule can either rotate clockwise or counterclockwise. Neither of the two pathways can be excluded and hence the unidirectionality of rotation of the system is not certain. However, the system performs its three-state cycle with high selectivity. Starting with the stable *cis*-**5**, irradiation leads to full conversion into unstable *cis*-**5** in the first step of the rotary process. Subsequent heating or irradiation of unstable *cis*-**5** gives solely stable *trans*-**5**. The system reverts eventually to the original *cis*-**5** on prolonged heating of stable *trans*-**5** at high temperatures. The molecule therefore represents a three-state switching system. In conclusion, the alkene **5** not only offers new insights in the behavior of the molecular motors, but also provides an interesting showcase for the stereochemistry of very hindered alkenes in general.

## Experimental

### General information

The high-resolution one- and two-dimensional $^1$H NMR spectra were obtained using a Varian VXR-300 and a Varian Mercury Plus operating at 299.97 and 399.93 MHz, respectively, for the $^1$H nucleus. $^{13}$C NMR spectra were recorded on a Varian VXR-300 and a Varian Mercury Plus operating at 75.43 and 100.57 MHz, respectively. Chemical shifts in $^1$H spectra are reported in $\delta$ units (ppm) relative to the residual non-deuterated solvent signals: $CHCl_3$ ($\delta$ 7.26 ppm), benzene ($\delta$ 7.15 ppm) toluene ($\delta$ 2.08 ppm). Chemical shifts in $^{13}$C spectra are reported in $\delta$ units (ppm) relative to the deuterated solvent signals: $CDCl_3$ ($\delta$ 77.0 ppm), benzene-$d_6$ ($\delta$ 128.0 ppm). The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). All coupling constants ($J$) are denoted in Hertz (Hz). One-dimensional $^1$H NMR spectra were recorded using the acquisition parameters: $\pi/2$ pulse width, 6.5 µs; spectral width, 6.000 Hz; data size, 16 K; recycling delay, 1 s; number of transients, 32; temperature 298 K. COSY, clean-TOCSY (MLEV-17), NOESY and HMQC experiments were used for the assignment of the $^1$H and $^{13}$C NMR resonances when required. Melting points were taken on a Mettler FP-2 melting point apparatus, equipped with a Mettler FP-21 microscope and are uncorrected. Optical rotations were measured with a Perkin Elmer 241 Polarimeter. UV-Vis measurements were performed on a Hewlett-Packard HP 8453 FT spectrophotometer and CD spectra were recorded on a JASCO J-715 spectropolarimeter using Uvasol grade solvents (Merck). MS (EI) and HRMS (EI) spectra were obtained with a Jeol JMS-600 spectrometer. Column chromatography was performed using silica gel (Aldrich 60, 230–400 mesh). HPLC analyses were performed on a Shimadzu HPLC system equipped with two LC-10AD*vp* solvent delivery systems, a DGU-14A degasser, a SIL-10AD*vp* autosampler, a SPD-M10A UV/Vis photodiode array detector, a CTO-10A*vp* column oven and a SCL-10A*vp* controller unit using a Chiralcel OD (Daicel) column. Preparative HPLC was performed on a Gilson HPLC system consisting of a 231XL sampling injector, a 306 (10SC) pump, an 811C dynamic mixer, a 805 manometric module, with a 119 UV/Vis detector and a 202 fraction collector, using the Chiralcel OD (Daicel) column. Elution speed was 1 ml min$^{-1}$. Solvents were distilled and dried before use by standard methodology. Irradiation experiments were performed with a 180 W Oriel Hg-lamp using a pyrex filter or filters of the appropriate wavelengths. Photostationary states were ensured by monitoring composition changes in time by taking UV-Vis spectra at certain intervals until no changes were observed. Thermal helix inversions were monitored by CD spectroscopy using the apparatus described above and a JASCO PFD-350S/350L Peltier type FDCD attachment with a temperature control.

### Calculations

All semiempirical calculations have been performed using an AM1 Hamiltonian employing the CaChe WS Pro 5.0 software.[19] The ground state geometries were fully optimised with the use of b3lyp hybrid functional and 3-21g(d) basis set. For all DFT-calculated structures the single-point energy were calculated at b3lyp/6-31g(d) level. In our computations all excited-state calculations have been performed based upon the ground state geometries of single molecules with the use of a Gaussian program package.[20]

**(2*S**,2′*S**)-(*P**,*P**)-*cis*-(±)-2,2′-Di-*tert*-butyl-2,2′,3,3′-tetrahydro-1,1′-bicyclopenta[*a*]naphthalenylidene (5).** To a stirred suspension of zinc powder (1.0 g, 15.3 mmol) in THF (10 ml) was added carefully at 0 °C under an argon atmosphere $TiCl_4$ (0.85 ml, 1.5 g, 7.7 mmol). The resulting black slurry was refluxed for 2 h.

Ketone **11** (0.92 g, 3.87 mmol) was added and heating at reflux was continued for 13 d. The reaction mixture was then poured into a saturated aqueous solution of $NH_4Cl$ (100 ml) and extracted with ethyl acetate (3 × 50 ml). The organic layers were dried ($MgSO_4$) and the solvents were removed under reduced pressure giving a yellow oil. This oil was further purified by column chromatography ($SiO_2$, heptane, $R_f = 0.30$) providing the *cis* and *trans* alkenes **5** as a yellow solid in an approximate *cis*:*trans* ratio of 5 : 2 (160 mg, 0.36 mmol, 19%); *m*/*z* (EI, %) = 444 ($M^+$, 64), 387 (49), 331 (100); HRMS (EI): calc. for $C_{34}H_{36}$: 444.2817, found: 444.2809. The *cis*-**5**-isomer was obtained pure as an amorphous white solid by precipitation from heptane. Crystals suitable for X-ray analysis were obtained as thin colorless platelets by recrystallisation from heptane; mp 223.5–224.2 °C. Stable (2S*,2′S*)-(P*,P*)-*cis*-**5**: $^1$H (300 MHz, $CDCl_3$) δ 0.79 (s, 18H), 2.94 (d, 15.4, 2H), 3.43 (dd, 15.4, 5.9, 2H), 3.61 (d, 5.9, 2H), 6.28–6.38 (m, 4H), 6.84–6.89 (m, 2H), 7.43 (d, 8.1, 2H), 7.54 (d, 8.4, 2), 7.63 (d, 8.1, 2H); $^1$H (400 MHz, toluene-$d_8$) δ 0.81 (s, 18H, $t\mathrm{Bu}_{2ax}$), 2.82 (d, 15.2, 2H, $H_{3ax}$), 3.34 (dd, 15.2, 5.8, 2H, $H_{3eq}$), 3.63 (d, 5.8, 2H, $H_{2eq}$), 6.30–6.34 (m, 2H, $H_8$), 6.61 (d, 8.1, 2H, $H_9$), 6.74 (m, 2H, $H_7$), 7.30 (d, 8.1, 2H, $H_4$), 7.41 (d, 8.1, 2H, $H_6$), 7.54 (d, 8.1, 2H, $H_5$); $^1$H (400 MHz, benzene-$d_6$, spectral data derived from a mixture containing *trans*-**5**) δ 0.82 (s, 18H), 2.82 (d, 15.4, 2H), 3.34 (dd, 15.4, 6.2, 2H), 3.64 (d, 6.2, 2H), 6.37–6.41 (m, 2H), 6.70 (d, 8.1, 2H) 6.75–6.79 (m, 2H), 7.32 (d, 8.1, 2H), 7.46 (d, 8.1, 2H), 7.57 (d, 8.1, 2H);$^{13}$C (75 MHz, $CDCl_3$) δ 28.7 (q), 34.5 (s), 35.1 (t), 58.8 (d), 122.3 (d), 123.8 (d), 123.9 (d), 126.2 (d), 127.4 (d), 128.1 (d), 128.4 (s), 132.1 (s), 139.1 (s), 140.1 (s), 144.0 (s); UV-Vis: (*n*-hexane) $\lambda_{max}$/nm ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 227 (76 100), 254 (28 700), 307 (10 000), 327 (8600), 362 (12 700). Resolution of stable *cis*-**5** was performed by chiral HPLC using a Daicel Chiralcel OD column as the stationary phase and a mixture of heptane–isopropyl alcohol in a ratio of 99.75 : 0.25 as the eluent at a rate of 1 ml min$^{-1}$. The first eluted fraction ($t$ = 4.08 min) of *cis*-**5** contained (2*S*,2′*S*)-(*P*,*P*)-*cis*-**5**, the second fraction ($t$ = 4.92 min) contained (2*R*,2′*R*)-(*M*,*M*)-*cis*-**5**; (2*S*,2′*S*)-(*P*,*P*)-*cis*-**5**: CD: (*n*-hexane) $\lambda_{max}$/nm ($\Delta\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 225.8 (+68.1), 233.6 (−214.8), 267.6 (+253.4), 376.4 (+4.6).

**(2S*,2′S*)-(P*,P*)-*trans*-(±)-2,2′-Di-*tert*-butyl-2,2′,3,3′-tetrahydro-1,1′-bicyclopenta[*a*]naphthalenylidene (5).** Not obtained in pure form from synthesis as described above. The stable *trans*-**5** was obtained pure *via* photochemical isomerisation methods. This involves either irradiation ($\lambda \geq 280$ nm, $T = 0$ °C) of (2*S*,2′*S*)-(*P*,*P*)-*cis*-**5** in *n*-hexane to form the unstable (2*S*,2′*S*)-(*M*,*M*)-*cis*-**5** followed by irradiation with a different wavelength ($\lambda \geq 436$ nm, $T = 0$ °C) or by irradiation ($\lambda \geq 280$ nm, $T = 0$ °C) of (2*S*,2′*S*)-(*P*,*P*)-*cis*-**5** in dodecane to form the unstable (2*S*,2′*S*)-(*M*,*M*)-*cis*-**5** which is then converted to the stable (2*S*,2′*S*)-(*P*,*P*)-*trans*-**5** by heating at elevated temperatures; $^1$H (300 MHz, $CDCl_3$, spectral data derived from a mixture containing *cis*-**5**) δ 0.81 (s, 18H), 2.42 (d, 15.0, 2H), 2.56 (dd, 15.0, 5.5, 2H), 3.00 (d, 5.5, 2H), 7.25 (d, 7.3, 2H), 7.41–7.55 (m, 4H), 7.68 (d, 8.4, 2H), 7.86 (d, 8.1, 2H), 8.52 (d, 8.1, 2H); $^1$H (400 MHz, benzene-$d_6$, spectral data derived from a mixture containing *cis*-**5**) δ 0.88 (s, 18H), 2.21 (d, 15.0, 2H), 2.47 (dd, 15.0, 5.5, 2H), 3.18 (d, 5.5, 2H), 7.07 (d, 8.1, 2H), 7.24–7.28 (m, 2H), 7.39–7.44 (m, 2H), 7.52 (d, 8.1, 2H), 7.69 (d, 8.1, 2H), 8.72 (d, 8.4, 2H); $^1$H (400 MHz, toluene-$d_8$) δ 0.86 (s, 18H, $t\mathrm{Bu}_{2ax}$), 2.22 (d, 15.0, 2H, $H_{3ax}$), 2.47 (dd, 15.0, 5.5, 2H, $H_{3eq}$), 3.13 (d, 5.5, 2H, $H_{2eq}$), 7.05 (d, 8.1, 2H, $H_4$), 7.22–7.26 (m, 2H, $H_7$), 7.37–7.40 (m, 2H, $H_5$), 7.49 (d, 8.4, 2H, $H_8$), 7.64 (d, 8.4, 2H, $H_6$), 8.67 (d, 8.4, 2H, $H_9$); $^{13}$C (75 MHz, $CDCl_3$) δ 29.7 (q), 34.0 (s), 34.7 (t), 57.7 (d), 122.9 (d), 124.6 (d), 124.7 (d), 127.2 (d), 127.9 (d), 128.3 (d), 129.0 (s), 132.9 (s), 140.9 (s), 141.3 (s), 143.0 (s); UV-Vis: (*n*-hexane) $\lambda_{max}$/nm ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 209 (115 000), 223 (88 700), 235 (35 700), 239 (35 100), 276 (11 300), 349 (19 700), 364 (22 100). Resolution of stable *trans*-**5** was performed by chiral HPLC on a analytical scale using a Daicel Chiralcel OD column as the stationary phase and a mixture of heptane–isopropyl alcohol in a ratio of 99.75 : 0.25 as the eluent at a rate of 1 ml min$^{-1}$. The first eluted fraction ($t$ = 4.41 min) of *trans*-**5** contained (2*S*,2′*S*)-(*P*,*P*)-*trans*-**5**, the second fraction ($t$ = 5.39 min) contained (2*R*,2′*R*)-(*M*,*M*)-*trans*-**5**; (2*S*,2′*S*)-(*P*,*P*)-*trans*-**5**: CD: (*n*-hexane): $\lambda_{max}$/nm ($\Delta\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 216.6 (+136.4), 222.8 (−74.8), 229.0 (+50.4), 242.0 (−19.0), 250.2 (+46.0), 252.6 (+35.0), 259.2 (+158.7), 268.0 (+28.9), 278.6 (36.3), 326.6 (−11.8), 334.4 (−6.4), 346.6 (−19.6), 354.6 (−15.8), 362.2 (−21.8).

**(2S*,2′S*)-(M*,M*)-*cis*-(±)-2,2′-Di-*tert*-butyl-2,2′,3,3′-tetrahydro-1,1′-bicyclopenta[*a*]naphthalenylidene (5).** The compound was obtained pure form by photochemical conversion. Preparation was performed by irradiation of the either pure (2*S*,2′*S*)-(*P*,*P*)-*cis*-**5** in *n*-hexane ($\lambda \geq 280$ nm, $T = 0$ °C), or a mixture of racemic *cis*-**5** or *trans*-**5** in benzene-$d_6$ and toluene-$d_8$ at room temperature; $^1$H (400 MHz, $CDCl_3$) δ 0.97 (s, 18H), 3.24–3.34 (m, 4H), 3.63 (d, 7.0, 2H), 6.46–6.51 (m, 2H), 7.03–7.07 (m, 2H), 7.29 (d, 8.1, 2H), 7.43 (d, 8.1, 2H), 7.65 (d, 7.7, 2H), 7.71 (d, 8.1, 2H); $^1$H (400 MHz, toluene-$d_8$) δ 0.96 (s, 18H), 3.17–3.20 (m, 4H), 3.60–3.62 (m, 2H), 6.39–6.44 (m, 2H), 6.83–6.87 (m, 2H), 7.256 (d, 8.1, 2H), 7.49 (d, 8.4, 2H), 7.55 (d, 8.1, 2H), 7.63 (d, 8.1, 2H); $^1$H (400 MHz, benzene-$d_6$) δ 0.98 (s, 18H, $t\mathrm{Bu}_{2eq}$), 3.19–3.22 (m, 4H, $H_{3ax}$, $H_{3eq}$), 3.61–3.64 (m, 2H, $H_{2ax}$), 6.42–6.47 (m, 2H, $H_8$), 6.85–6.90 (m, 2H, $H_7$), 7.28 (d, 8.1, 2H, $H_4$), 7.55 (d, 8.1, 2H, $H_5$), 7.60 (d, 8.1, 2H, $H_6$), 7.74 (d, 8.4, 2H, $H_9$); $^{13}$C (100 MHz, $CDCl_3$) δ 27.9 (q), 29.8 (s), 30.2 (t), 55.6 (d), 123.1 (d), 124.8 (d), 124.9 (d), 129.0 (d), 130.2 (s), 133.9 (s), 139.2 (s), 143.9 (s), 148.2 (s); two (d) were missing due to overlap with the toluene-$d_8$; *m*/*z* (EI, %) = 444 ($M^+$, 43), 387 (45), 331 (100). UV-Vis: (*n*-hexane) $\lambda_{max}$/nm ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 227 (70 000), 289 (19 100), 324 (9700), 481 (16 100); The retention time of unstable (2*S*, 2′*S*)-(*M*,*M*)-*cis*-**5** is $t$ = 11.36 min using a Daicel Chiralcel OD column as the stationary phase and a mixture of heptane–isopropyl alcohol in a ratio of 99.75 : 0.25 as the eluent at a rate of 1 ml min$^{-1}$; (2*S*,2′*S*)-(*M*,*M*)-*cis*-**5**: CD: (*n*-hexane): $\lambda_{max}$/nm ($\Delta\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 205.8 (+113.5), 223.0 (−157.7), 236.6 (+44.6), 262.4 (−9.5), 284.6 (+43.5), 303.0 (−8.8), 307.6 (−4.7), 327.0 (−12.5).

**3,3-Dimethylbutyric acid methyl ester (7).** A mixture of 3,3-dimethylbutyric acid **6** (24 g, 0.21 mol), DMF (150 ml), methyl iodide (20 ml) and $K_2CO_3$ (25 g) was stirred overnight at room temperature. Addition of diethyl ether (100 ml) and subsequent thorough washing with water (6 × 200 ml) gave after drying ($MgSO_4$) and removal of the diethyl ether the crude ester. For further purification ester **7** was distilled at atmospheric pressure to yield a colorless liquid (23 g, 0.18 mol, 86%); bp 129–132 °C (lit.[21] 124–128 °C); $^1$H (300 MHz, $CDCl_3$) δ 1.02 (s, 9H), 2.2 (s, 2H), 3.65 (s, 3H); $^{13}$C (75 MHz, $CDCl_3$) δ 29.5 (q), 30.5 (s), 47.6 (t), 50.9 (q), 172.6 (s).

**3,3-Dimethyl-2-naphthalen-2-ylmethylbutyric acid methyl ester (9).** A freshly prepared solution of LDA (16 mmol) in THF (50 ml) was cooled to −70 °C and neat methyl 3,3-dimethylbutanoate (1.95 g, 15 mmol) was added. The mixture was stirred for 45 min while maintaining the temperature at approximately −70 °C. A solution of the bromide **8** (6.6 g, 30 mmol) dissolved in THF (30 ml) was added at −70 °C and allowed to react while stirring overnight. After quenching with an aqueous saturated solution of $NH_4Cl$ (100 ml), the reaction mixture was extracted with diethyl ether (3 × 75 ml). The combined organic layers were washed with water and the solid remaining after evaporation of all volatiles was purified using column chromatography ($SiO_2$, heptane–ethyl acetate = 50 : 1, $R_f = 0.24$) yielding the ester **9** as a colorless solid (2.7 g, 10 mmol, 67%); mp 69.6–70.5 °C; $^1H$ (300 MHz, $CDCl_3$) $\delta$ 1.12 (s, 9H), 2.62 (dd, 11.7, 3.7, 1H), 2.97–3.14 (m, 2H), 3.47 (s, 3H), 7.31 (dd, 8.4, 1.5, 1H), 7.41–7.49 (m, 2H), 7.62 (s, 1H), 7.75–7.82 (m, 3H); $^{13}C$ (75 MHz, $CDCl_3$) $\delta$ 27.7 (q), 33.0 (t), 34.0 (s), 50.5 (q), 58.4 (d), 125.1 (d), 125.7 (d), 126.8 (d), 127.1 (d), 127.3 (d), 127.4 (d), 127.8 (d), 132.0 (s), 133.4 (s), 137.6 (s), 174.7 (s); *m*/*z* (EI, %) = 270 ($M^+$, 67), 214 (41), 181 (71), 141 (100); HRMS (EI): calc. for $C_{18}H_{22}O_2$: 270.1620, found: 270.1614.

**3,3-Dimethyl-2-naphthalen-2-ylmethylbutyric acid (10).** A mixture of ester **9** (2.7 g, 10 mmol), ethanol (50 ml) water (50 ml) and KOH (5.0 g, 89 mmol) was refluxed for 6 days. Acidification with an aqueous solution of 30% HCl, subsequent extraction with diethyl ether (3 × 50 ml) and washing of the combined organic layers with water, gave after drying ($MgSO_4$) and evaporation of all volatiles acid **10** as a yellow, impure solid. This solid was recrystallised from a mixture of heptane–ethyl acetate = 50 : 1 to give the desired acid **10** as a white solid (2.1 g, 8.2 mmol, 82%); mp 113.9–115.2 °C; $^1H$ (300 MHz, $CDCl_3$) $\delta$ 1.09 (s, 9H), 2.58 (dd, 9.0, 5.3, 1H), 2.99–3.03 (m, 2H), 7.26–7.43 (m, 3H), 7.61 (s, 1H), 7.70–7.75 (m, 3H); $^{13}C$ (75 MHz, $CDCl_3$) $\delta$ 27.7 (q), 32.8 (t), 33.9 (s), 58.3 (d), 125.1 (d), 125.7 (d), 126.9 (d), 127.1 (d), 127.5 (2 × d), 127.9 (d), 132.1 (s), 133.5 (s), 137.4 (s), 179.7 (s); *m*/*z* (EI, %) = 256 ($M^+$, 51), 200 (34), 141 (100); HRMS (EI): calc. for $C_{17}H_{20}O_2$: 256.1463, found: 256.1470.

**2-*tert*-Butyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-one (11).** A mixture of acid **10** (1.96 g, 7.7 mmol), $SOCl_2$ (2.1 ml, 29 mmol) and DMF (2 drops) in $CH_2Cl_2$ (100 ml) was refluxed for 1 h. All volatiles were then removed under reduced pressure and the yellow oil remaining was dissolved in 1,2-dichloroethane (75 ml) and cooled to 0 °C. $AlCl_3$ (2.0 g, 15 mmol) was added portionwise and the reaction mixture turned deep green. After stirring for 1 h, the reaction was quenched by addition of an aqueous solution of 1 M HCl (100 ml) followed by extraction with $CH_2Cl_2$ (2 × 50 ml). The oil remaining after removal of all volatiles under reduced pressure was purified by using a short column ($SiO_2$, heptane–ethyl acetate = 16 : 1, $R_f = 0.50$). The ketone **11** was obtained as a slightly yellow oil which solidified upon standing (1.53 g, 6.4 mmol, 84%); mp 71.9–73.2 °C; $^1H$ (300 MHz, $CDCl_3$) $\delta$ 1.10 (s, 9H), 2.60 (dd, 7.3, 3.7, 1H), 3.08 (dd, 17.9, 3.7, 1H), 3.28 (dd, 17.9, 7.3, 1H), 7.49–7.57 (m, 2H), 7.64–7.69 (m, 1H), 7.89 (d, 8.1, 1H), 8.03 (d, 8.4, 1H), 9.18 (d, 8.4, 1H); $^{13}C$ (75 MHz, $CDCl_3$) $\delta$ 27.5 (q), 30.1 (t), 33.7 (s), 56.8 (d), 123.6 (d), 123.8 (d), 126.2 (d), 128.0 (d), 128.6 (d), 129.2 (s), 131.5 (s), 132.5 (s), 135.3 (d), 156.3 (s), 208.3 (s); *m*/*z* (EI, %) = 238 ($M^+$, 18), 182 (100); HRMS (EI): calc. for $C_{17}H_{18}O$: 238.1358, found: 238.1371.

**2,2′-Di-*tert*-butyl-3*H*,3′*H*-[1,1′]bi(cyclopenta[*a*]naphthalenyl) (12).** This compound (1.2 mg, 2.7 μmol) was isolated by column chromatography ($SiO_2$, heptane, $R_f = 0.45$) after the photochemical isomerisation reaction of olefin **5**; $^1H$ (400 MHz, $CDCl_3$) $\delta$ 1.14 (s, 18H), 3.71 (d, 23.1, 2H), 3.81 (d, 23.1, 2H), 6.95–6.99 (m, 2H), 7.20–7.24 (m, 2H), 7.65–7.68 (m, 4H), 7.79 (d, 8.4, 2H), 7.94 (d, 8.4, 2H); $^1H$ (400 MHz, toluene-$d_8$) $\delta$ 1.12 (s, 18H), 3.45 (d, 23.1, 2H), 3.59 (d, 23.1, 2H), 6.75–6.79 (m, 2H), 7.50 (d, 8.2, 2H), 7.58 (d, 8.2, 2H), 7.62 (d, 7.3, 2H), 8.20 (d, 8.8, 2H); one (m, 2H) was not observed due to overlap with the solvent. $^{13}C$ (100 MHz, $CDCl_3$) $\delta$ 29.7 (q), 31.0 (t), 109.7 (d), 121.9 (d), 123.8 (d), 125.0 (d), 125.1 (d), 128.4 (d), no (s) were observed due to small amount of material obtained. *m*/*z* (EI, %) = 442 ($M^+$, 100), 427 (47); HRMS (EI): calc. for $C_{34}H_{34}$: 442.2661, found: 442.2653.

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7 The use of an asterisk (*) throughout this paper denotes the use of racemic compounds and is used to clarify the relation between the helicity of the molecule and the absolute configuration of the carbon atom of the stereogenic center. For example, for an alkene with a methyl substituent, (2*R**,2′*R**)-(*P**,*P**)-*trans* means that the alkene is a racemic mixture of two enantiomers, (2*R*,2′*R*)-(*P*,*P*)-*trans* and (2*S*,2′*S*)-(*M*,*M*)-*trans*, of a stable *trans*-isomer, whereas for the same alkene, (2*R**,2′*R**)-(*M**,*M**)-*trans* would indicate that the molecule is a racemic mixture of an unstable *trans*-isomer consisting of the (2*R*,2′*R*)-(*M*,*M*)-*trans* and (2*S*,2′*S*)-(*P*,*P*)-*trans* enantiomers. From this example, it is important to note that a combination of the absolute configuration at the stereogenic carbon atom (*R* or *S*) and the overall helicity of the molecule (*P* or *M*) is only valid for certain combinations, because different isomers, stable or unstable, can be meant. Furthermore, it

should be noted that the overall conformation of the (2*S**,2′*S**)-(*P**,*P**)-*tert*-butyl substituted alkene **5** is identical to that (2*R**,2′*R**)-(*P**,*P**)-methyl substituted alkene **4**. Due to a change in the priority of the substituents attached to the stereogenic center, the absolute configuration alters.

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9 *Crystal data* for (2*S**,2′*S**)-(*P**,*P**)-*cis*-**5**: $C_{34}H_{36}$, $M_r$ = 444.66, orthorhombic, *Pbca*, $a$ = 7.2761(3), $b$ = 19.4524(8), $c$ = 36.240(1) Å, $V$ = 5129.3(3) Å$^3$, $Z$ = 8, $D_c$ = 1.152 g cm$^{-3}$, $T$ = 100(1) K, numberof reflections: 6334; number of refined parameters: 451; final agreement factors: $wR(F^2)$ = 0.1230, $R(F)$ = 0.0475, GooF = 1.030. CCDC reference number 271758. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611070c.

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11 *Crystal data* for (2*S**,2′*S**)-(*M**,*M**)-*cis*-**5**: $C_{34}H_{36}$, $M_r$ = 444.66, orthorhombic, $P2_12_12_1$, $a$ = 9.7582(6), $b$ = 14.4454(8), $c$ = 17.915(1) Å, $V$ = 2525.3(3) Å$^3$, $Z$ = 4, $D_c$ = 1.169 g cm$^{-3}$, $T$ = 100(1) K, number of reflections: 4973; number of refined parameters: 451; final agreement factors: $wR(F^2)$ = 0.0838, $R(F)$ = 0.0341, GooF = 1.049. CCDC reference number 271759. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611070c.

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