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The Stereochemical Course of the Generation and Interception of a Six-Membered Cyclic Allene: 3δ²-1*H*-Naphthalene (2,3-Didehydro-1,2-dihydronaphthalene)[‡]

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

Keywords: CD spectra / Cycloadditions / Cyclic allenes / Enantioselectivity / Quantum chemistry calculations

The bromofluorocarbene adduct *rac*-**1** of indene, possessing the fluorine atom at the *endo* position, is a useful substrate for the generation of the isonaphthalene **4** by the Doering–Moore–Skattebøl reaction. By resolution of *rac*-**1**, an enantiomerically pure precursor of a six-membered cyclic allene was obtained for the first time. The treatment of (+)- or (–)-**1**, dissolved in 2,5-dimethyl-, 2-*tert*-butyl-5-methyl-, or 2,5-bis(*tert*-butyl)furan, with methyllithium gave rise to the [4+2] cycloadducts **6** of **4** to the furans. It was shown by means of HPLC on Chiralcel OD that the formation of **6** proceeded with about 40 % *ee*, and that this value was independent of the type and concentration of the furan, and the reaction temperature. The absolute configurations of the enantiomers **1**, as well as those of the enantiomers **6**, were determined by simulation of the CD spectra by quantum chemical methods and by the comparison of them with the experimental spectra. In the case of (+)-**1**, the reliability of this procedure was checked by X-ray crystal structure analysis. On the basis of these results, a model is proposed for the steric course of the reaction sequence, leading from a pure enantiomer **1** to the 70:30 mixtures of the product enantiomers **6**. The use of indene as trapping reagent for **4** furnished the [2+2] cycloadduct **15**. For the preparation of *rac*-**15**, the particularly simple one-pot procedure was employed, in which indene, tetrabromomethane, and methyllithium were combined and in which the dibromocarbene adduct **2** of indene serves as precursor of **4**. Compound **2** could not be isolated, but was characterised by low-temperature ^{1}H NMR spectra. The conversion of (+)- or (–)-**1** into **4** in the presence of indene afforded **15** only with a very low enantioselectivity. The constitutions and the relative configurations of **15** as well as the compounds **8** and **16**, which resulted from thermolysis of the cycloadducts **6b** and **15**, respectively, were elucidated by X-ray crystal diffraction.

Introduction

By elegant experiments, Balci and Jones[1,2] established the chirality of the six-membered cyclic allenes[3] 1,2-cyclohexadiene and bicyclo[3.2.1]octa-2,3,6-triene. Later, quantum chemical calculations corroborated that the ground state of 1,2-cyclohexadiene has the allene structure, whereas the corresponding allyl diradical, being 15–18 kcal mol^{-1} higher in energy, serves as the transition state for the enantiomerisation.[4,5] The barrier to enantiomerisation of the title allene **4** (Scheme 1) was calculated to be significantly lower, namely 11 kcal mol^{-1}.[5] If a nitrogen or an oxygen atom is directly attached to the allene subunit within a six-membered ring, this barrier is predicted to have a considerably smaller value or may even vanish.[3,5–8] We now report that, in spite of the rather low barrier to enantiomerisation, enantioselectively generated **4** can be trapped by activated olefins before racemisation occurs.

Our approach to the problem consists in the utilisation of a chiral precursor to the isonaphthalene **4**. Previously, **4** was generated from the bromofluorocarbene adduct *rac*-**1**[9,10] of indene, the dibromocarbene adduct **2**[10] of indene,

[‡] Cycloallenes, Part 20. Ref.[3] is counted as Part 19. For Part 18, see ref.[7].

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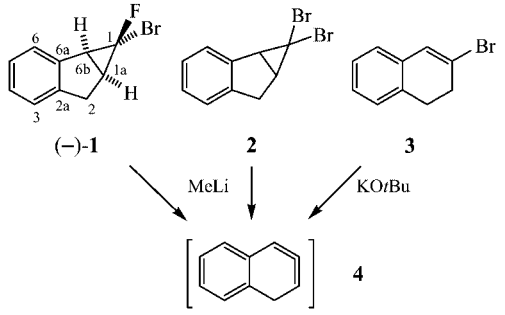


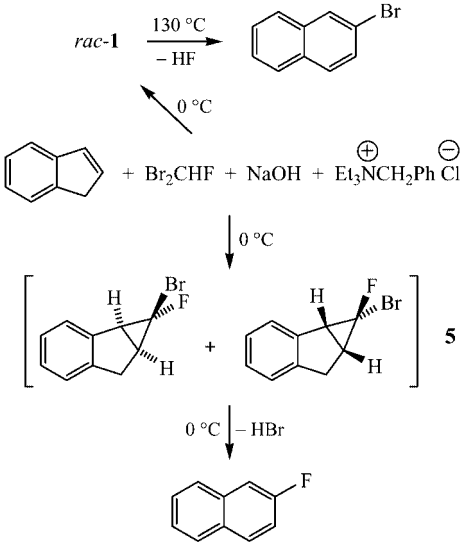
Scheme 1. Precursors to the isonaphthalene **4**.

and from 3-bromo-1,2-dihydronaphthalene (**3**)[11] (Scheme 1). As **3** is achiral and **2** cannot be isolated (see section 4), only *rac*-**1** suited our goal.

Results and Discussion

1. Preparation of the Precursor *rac*-1 of the Cyclic Allene 4, Resolution of *rac*-1, Generation of 4 from the Pure Enantiomers (+)-1 and (–)-1 and Trapping of 4 by Furans

The preparation of *rac*-**1** is described here in detail. Previously, it has only briefly been mentioned in a conference report[9] and a communication.[10] Exposure of indene to a mixture of dibromofluoromethane and sodium hydroxide in dichloromethane containing benzyltriethylammonium chloride gave rise to a 15% yield of *rac*-**1** (Scheme 2). The rather modest yield is a consequence of the simultaneous formation of the diastereomers **5** of *rac*-**1**, which cannot be isolated due to their rapid conversion into 2-fluoronaphthalene by ejection of the bromide ion with concomitant ring expansion and final loss of a proton. Our workup was not



Scheme 2. The addition of bromofluorocarbene to indene and the conversion of the adducts *rac*-**1** and -**5** into 2-bromo- and 2-fluoronaphthalene, respectively.

designed for the observation of 2-fluoronaphthalene, but previous papers describe its preparation from indene and halofluorocarbenes.[12]

Compared to **5**, the greater stability of *rac*-**1** is explained by the stereoelectronic requirements of the ring expansion,[13] which demand the ejection of a fluoride ion. However, the strength of the C–F bond, whose bond dissociation energy is ca. 40 kcal mol^{-1}[14] larger than that of a C–Br bond, inhibits this step at 20 °C and permits it only at 130 °C, at which temperature 2-bromonaphthalene emerges from *rac*-**1** (Scheme 2).

The attainment of the pure enantiomers from *rac*-**1** was achieved by HPLC on Chiralcel OD. An X-ray crystal structure analysis [Flack parameter = –0.003(8)] established the 1*S*,1a*R*,6b*R*-configuration of (+)-**1** (Figure 1).

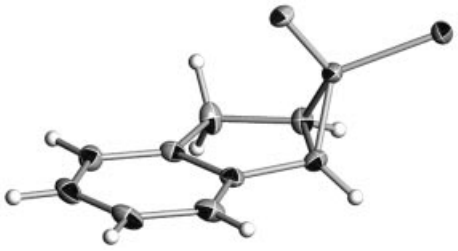
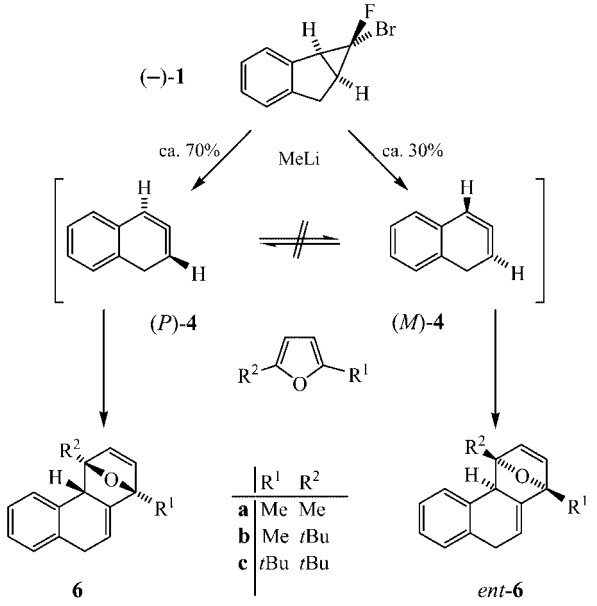


Figure 1. Molecular structure of (+)-**1**. The anisotropic displacement parameters are depicted at the 50% probability level.

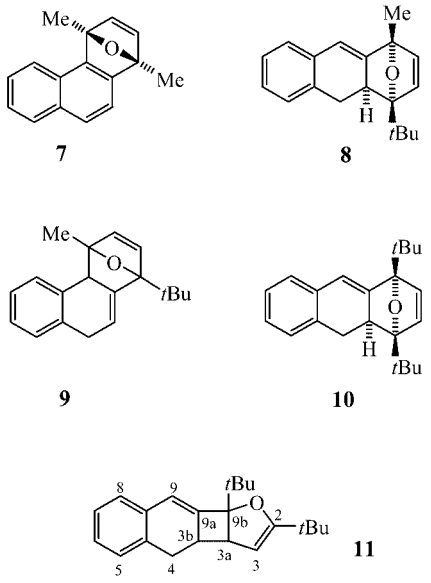
In order to trap the isonaphthalene **4**, generated from a pure enantiomer **1**, we chose 2,5-dimethylfuran as the first reagent. This diene furnished mainly one cycloadduct, namely *rac*-**6a** in 8% yield, and its regioisomer in less than 1% yield, when **4** had been liberated from 3-bromo-1,2-dihydronaphthalene (**3**).[11] The other activated olefins used to trap **4**, except styrene and α-methylstyrene, gave rise to products consisting of several components in similar quantities.[3] Indeed, the reaction of *rac*-**1**, dissolved in pure 2,5-dimethylfuran, with methyllithium at –30 °C brought about a 40% yield of *rac*-**6a**. Whether or not *rac*-**6a** was accompanied by a small amount of its regioisomer, was not investigated.

The utilisation of the pure enantiomer (–)-**1** did not lead to the formation of *rac*-**6a**, but to **6a** and *ent*-**6a** in the ratio of 73:27 (Scheme 3). Due to the rather ready rearrangement of *rac*-**6a** to its regioisomer,[11] we did not carry out the analysis of the enantiomeric ratio directly, but after the dehydrogenation of **6a**/*ent*-**6a** by DDQ yielding the epoxyphenanthrenes **7**/*ent*-**7** (Scheme 4), the mixture of which was subjected to HPLC on Chiralcel OD. To establish which signal belonged to which enantiomer, that is, to determine the absolute configuration, we compared the experimental CD spectra with the calculated ones. The procedure is described in section 2. The same treatment of (+)-**1** as above gave rise to **6a** and *ent*-**6a** in the ratio of 28:72.

The fact that some of the stereochemical information of a pure enantiomer **1** is transferred to the cycloadducts **6a**/*ent*-**6a**, proves the chirality of the intermediate **4**. Simulta-



Scheme 3. Generation of the isonaphthalene **4** from the pure enantiomer (1*R*,1a*S*,6b*S*)-**1** [(–)-**1**] and interception of **4** by 2,5-disubstituted furans.



Scheme 4. Further products or consecutive products of the interception of **4** by 2,5-disubstituted furans.

neously, the following question arises: at which stage is about 30% of this stereochemical information lost? Does that leakage occur during the generation of **4** from a pure enantiomer **1** or by partial equilibration of (*M*)- and (*P*)-**4** via the corresponding diradical as transition state[5] or by a low selectivity in the cycloaddition of an enantiomer **4** onto 2,5-dimethylfuran?

We first addressed this problem by dilution of 2,5-dimethylfuran. In the above experiments, the enantiomer **1** was dissolved in the pure trapping reagent for **4** and treated with methyllithium, but now mixtures of 2,5-dimethylfuran and diethyl ether in the ratios 3:1 and 1:1 were employed. Under these conditions, the intermediate **4** should have a longer lifetime and hence a higher probability to undergo enantiomerisation than in the above experiments. However, the same enantiomeric ratios were observed, that is, **6a**/*ent*-**6a** = 72.5:27.5 from (–)-**1** in 2,5-dimethylfuran/diethyl ether, 3:1, and 27:73 from (+)-**1** in 2,5-dimethylfuran/diethyl ether, 1:1. These results exclude the conversion of (*P*)-**4** into (*M*)-**4** and vice versa under the reaction conditions and suggest an activation barrier to the cycloaddition of **4** that lies well below 11 kcal mol^{-1}.

A further experiment was conducted at room temperature, that is about 50 °C higher than in the above cases. Again, the ratio of **6a** and *ent*-**6a** determined after the reaction of (–)-**1** was 72:28. Like the results obtained with different concentrations of 2,5-dimethylfuran, this finding suggests that the allene **4** has a stable configuration in trapping experiments, which is inconsistent with the rationalisation of the observations by Balci and Jones in the cases of 1,2-cyclohexadiene and bicyclo[3.2.1]octa-2,3,6-triene.[1,2] Generating these allenes as nonracemic mixtures, the authors observed optically active cycloadducts of 1,3-diphenylisobenzofuran, if the reactions were carried out at 53 °C, but racemic products at 100 °C. They suggested that the racemisation of the allenes is faster than their interception at 100 °C, which does not apply at 53 °C. In view of the above independence of the **6a**/*ent*-**6a** ratio on the temperature, this explanation is likely to miss the point, as 1,2-cyclohexadiene has a higher barrier to enantiomerisation than the isonaphthalene **4** (15–18 kcal mol^{-1} for 1,2-cyclohexadiene[4,5] vs. 11 kcal mol^{-1} for **4**[5]). Bicyclo[3.2.1]octa-2,3,6-triene might have a barrier similar to that of **4**, because of the enhanced strain energy due to the rigidity of the bicyclic skeleton. Most probably, the effect noted by Balci and Jones reflects the temperature dependence of k_H/k_D in the elimination step of nonracemic 1-bromo-6-deuteriocyclohexene[1] and the enantioselectivity in the elimination of hydrogen bromide from 1-bromocyclohexene or 3-bromobicyclo[3.2.1]octa-2,6-diene by enantiomerically pure potassium menthoxide.[2]

Next, we turned to tests to see if the cycloaddition step of **4** is responsible for the partial loss of the stereochemical information introduced with (–)- or (+)-**1** and, thus, increased the steric demand of the trapping reagent. Our first choice was 2-*tert*-butyl-5-methylfuran. When utilised as the solvent for the reaction of *rac*-**1** with methyllithium, this compound gave rise to a 25% yield of *rac*-**6b**, *rac*-**8**, and **9** in the ratio of 5:1:2. A competition experiment showed that 2,5-dimethyl- and 2-*tert*-butyl-5-methylfuran trapped the intermediate **4** equally fast.

With regard to the analysis of the **6b**/*ent*-**6b** ratio with the utilisation of a pure enantiomer **1**, the procedure as in the case of **6a**/*ent*-**6a** was to no avail, as the treatment of *rac*-**6b**, employed as a mixture with *rac*-**8** and **9**, with DDQ did not afford the racemic epoxyphenanthrene analogous to *rac*-**7**. We then tried to simplify the 5:1:2 mixture of *rac*-**6b**, *rac*-**8**, and **9** by thermolysis. Akin to the rearrangement of *rac*-**6a** to the respective tetrahydroepoxyanthracene,[11] *rac*-**6b** was converted into *rac*-**8** with 68% yield on refluxing

in toluene, whereas **9** remained largely unchanged. When the product was subjected to HPLC on Chiralcel OD, a baseline separation of the peaks of **8** and *ent*-**8** was achieved.

The reaction of pure (+)-**1** with methyllithium in the presence of 2-*tert*-butyl-5-methylfuran and the subsequent thermolysis of the product furnished **8** and *ent*-**8** in the ratio of 34:66, which is also valid for **6b**/*ent*-**6b**. The fractions of pure **8** and *ent*-**8** were collected, and, after evaporation of most of the solvent, crystals grew in one of the samples on storage at –30 °C. An X-ray crystal structure analysis established the constitution and the relative configuration of **8**/*ent*-**8** (Figure 2), but not the absolute configuration, which was determined by the comparison of the experimental and calculated CD spectra (see section 2).

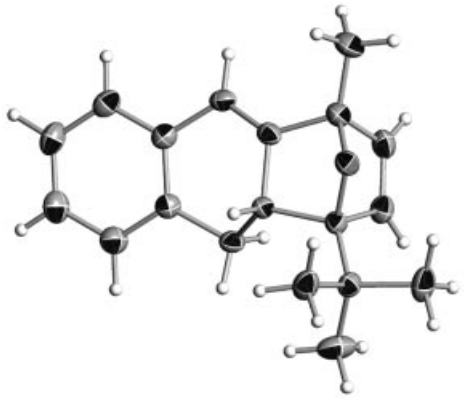


Figure 2. Molecular structure of **8**/*ent*-**8**. The anisotropic displacement parameters are depicted at the 50% probability level.

The loss of the stereochemical information introduced by pure enantiomer **1** was not very different for 2,5-dimethyl- and 2-*tert*-butyl-5-methylfuran as reaction partners of **4**. Therefore, we increased the steric demand of the trapping reagent further by utilising 2,5-di-*tert*-butylfuran. This heterocycle being the solvent in the treatment of *rac*-**1** with methyllithium gave rise to a 5:1 mixture of *rac*-**6c** (Scheme 3) and *rac*-**10** (Scheme 4). The similarity of their NMR spectroscopic data with those of *rac*-**6a**,**b** and *rac*-**8**, respectively, leaves no doubt as to the structure of *rac*-**6c** and *rac*-**10**. A yield of only 10% already indicated a relatively low reactivity of 2,5-di-*tert*-butylfuran toward the cycloallene **4**. Indeed, a competition experiment revealed that the relative rate constant is only one tenth of that of 2,5-dimethylfuran. In order to convert *rac*-**6c** into *rac*-**10** and hence to arrive at a uniform product, whose analysis of enantiomers would be simpler, we thermolysed the 5:1 mixture in refluxing benzene. Surprisingly, no *rac*-**10** at all was found in the product but only the formal [2+2] cycloadduct **11** of **4** onto 2,5-di-*tert*-butylfuran in 23% yield. Apparently, **11** is thermodynamically more stable than the formal [4+2] cycloadducts *rac*-**6c** and *rac*-**10**. As discussed previously, in the cases of the furan adducts of **4**[11] and 3δ^2-chromene (2,3-didehydro-2*H*-1-benzopyran),[15] a common racemic diradical (see **13**, Scheme 5 in section 3) should be the precursor to all three products. This diradical is believed to be first formed by attack of **4** with its central allene carbon atom at C-2 of the furan, and collapses to *rac*-**6** and *rac*-**10** under kinetic control at low temperature. It would be regenerated on heating of *rac*-**6** and *rac*-**10** and finally form a four-membered ring en route to **11**. In view of the rather modest yield and the insufficient purity of **11**, we decided to try the resolution directly with the 5:1 mixture of *rac*-**6c** and *rac*-**10** by HPLC on Chiralcel OD. Two signals of equal intensity were observed. According to the CD spectra, these originated from the minor components (**10** and *ent*-**10**), although the ratio of **6c** or *ent*-**6c** and **10** or *ent*-**10** was still about 5:1 for the material collected for each signal, as shown by the ^{1}H NMR spectra. It is detailed in the Exp. Sect. that these signals can also be used to quantify the relative amounts of **6c** and *ent*-**6c**. Thereupon, pure (+)-**1**, dissolved in 2,5-di-*tert*-butylfuran, was subjected to methyllithium, and the isolated product was analysed to contain **6c** and *ent*-**6c** in the ratio of 26:74.

In spite of the substantial difference in their steric demand, the allenophiles 2,5-dimethyl-, 2-*tert*-butyl-5-methyl- and 2,5-di-*tert*-butylfuran furnished enantiomeric mixtures of **6** and *ent*-**6** with the very similar ratios of 28:72, 34:66, and 26:74, respectively, on use of (+)-**1** as the substrate. This is why we conclude that the addition of an enantiomer **4** to each of the furans is highly stereoselective. Taking into account the above finding that the interconversion of the enantiomers **4** does not take place under the reaction conditions, we are left with the insight that the partial loss of the stereochemical information introduced with a pure enantiomer **1** already occurs during the generation of **4** from **1**. The small variation of the above ratios may be caused by the error limits of the analysis and/or by solvent effects of the different furans on the first step of the reaction sequences.

Previously, it has been shown that the liberation of 1-phenyl-1,2-cyclooctadiene from the enantiopure dibromocarbene adducts of 1-phenylcycloheptene proceeds with a high stereoselectivity.[16] In contrast, the Doering–Moore–Skattebøl reaction of an enantiomer **1** in the above furans brings about both enantiomers **4** in a ratio of about 70:30. Most likely, this divergence has its origin in the substitution pattern of the bridgehead positions of the cycloallene precursors. In the case of **1**, these positions (C-1a, C-6b) carry a hydrogen atom each, and with regards to the activation barriers, it does not make a big difference whether 1a-H or 6b-H of (–)-**1** moves to the other side of the ring system en route to (*P*)- or (*M*)-**4**, respectively (Scheme 3). However, the dibromocarbene adduct of 1-phenylcycloheptene has a hydrogen atom and a phenyl group at the bridgehead positions, and because of its steric demand the phenyl group might be strongly hindered in changing the ring side by the adjacent methylene group, whereas the hydrogen atom at the other bridgehead could smoothly undergo this movement.

For a more detailed consideration of the stereochemical course of the pathway from (+)- or (–)-**1** to **6** and *ent*-**6**, knowledge of the absolute configurations of the products is

necessary, which has been presented in advance in Scheme 3 and the corresponding discussion above. The elucidation of these absolute configurations is the subject of section 2.

2. Determination of Absolute Configurations by Calculation of the CD Spectra and Comparison with the Experimental Spectra

Circular dichroism (CD) is a chiroptical phenomenon, observed in nontransparent regions of the spectrum of nonracemic chiral compounds.[17] By resolving *rac*-**1**, *rac*-**7**, *rac*-**8**, and *rac*-**15** (see section 4), we obtained sufficient amounts of the enantiomers to measure CD spectra in the UV region. The fact that in all cases the spectrum of one enantiomer was almost the exact mirror image of that of the other is an indication of the purity of the substances, the structural identity of which was checked by NMR spectroscopy.

For the elucidation of the absolute configuration of a chiral compound, the simulation of its CD spectrum by quantum chemical methods and the comparison with the experimental spectrum is an established method.[17,18] The present calculations utilised the density functional theory and its time-dependent (TD) variant by applying the TURBOMOLE program package.[19] The geometries of the investigated compounds were optimised at the BLYP/SVP level[20–22] by applying the resolution of identity approximation[23,24] together with the matching auxiliary basis sets.[24,25] The electronic excitations were calculated at the TD-B3LYP[26–28] level of theory in combination with the TZVP basis sets.[29] For the molecules (–)-**1** and **6c**, the first 20 excitations were calculated, and for **7**, **8**, and **15**, the first 40 excitations. The UV spectra were simulated by superimposing Gauss functions, weighted according to the oscillator strength,[18] and then compared with the experimental spectra. With respect to the position of the strongest absorption, the calculated spectra of (–)-**1**, **7**, and **15** showed a hypsochromic shift of 15, 14, and 13 nm, respectively. In

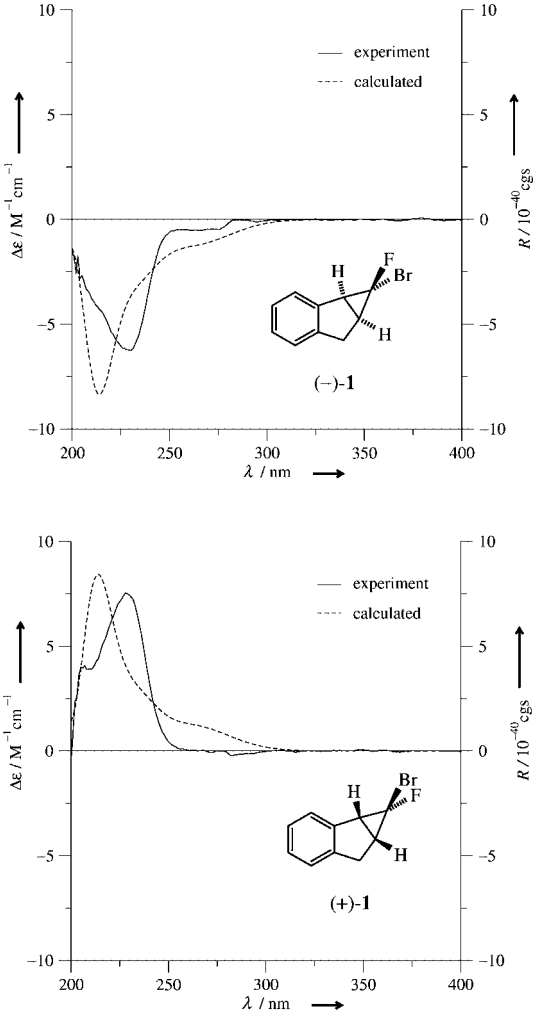


Figure 3. Comparison of the experimental and calculated (B3LYP) CD spectra of (–)-**1** (top) and (+)-**1** (bottom).

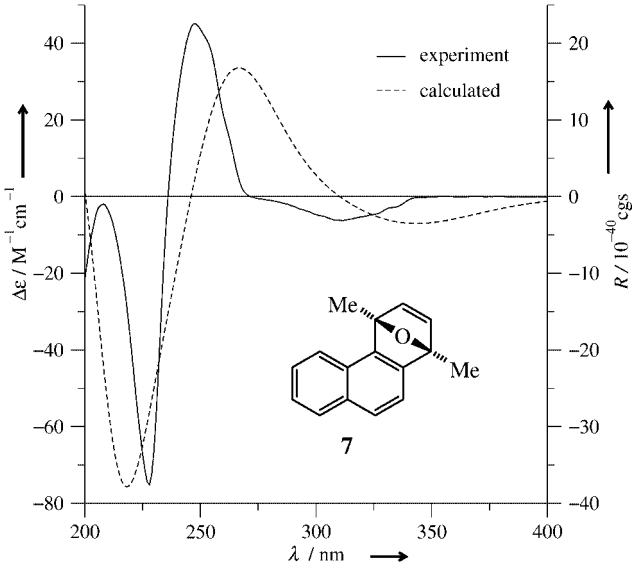


Figure 4. Comparison of the experimental and calculated (B3LYP) CD spectra of **7**.

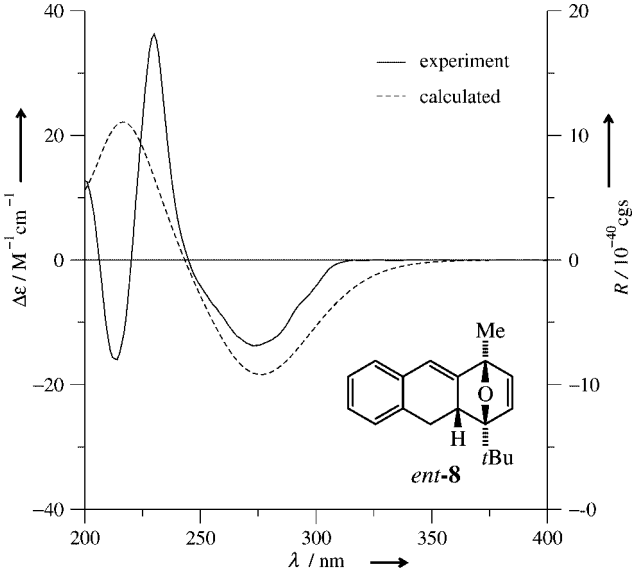


Figure 5. Comparison of the experimental and calculated (B3LYP) CD spectra of *ent*-**8**.

the case of **8**, the absorption maximum at lowest energy was used for comparison and found to be bathochromically shifted by 27 nm. The CD spectra were simulated by superimposing Gauss functions, weighted according to the rotator strength,[18] and then shifted by the number of wavelength units that corresponded to the deviation of the experimental and calculated UV spectra, given above. In Figures 3, 4, 5, and 6 the simulated CD spectra of (–)- and (+)-**1**, **7**, *ent*-**8**, and *ent*-**15** are compared with the matching experimental spectra, whereby the absolute configurations of the resolved samples were determined.

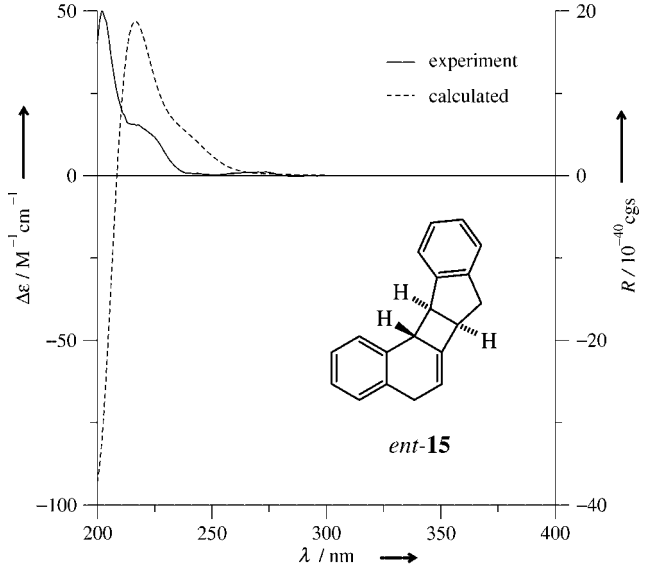
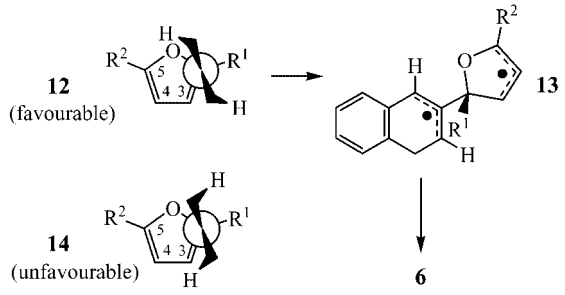


Figure 6. Comparison of the experimental and calculated (B3LYP) CD spectra of *ent*-**15**.

3. Proposal for the Stereochemical Course of the Generation of the Isonaphthalene 4 from 1 and Its Cycloaddition to Furans

Notwithstanding the knowledge of the absolute configuration of the precursor **1** for the intermediate **4** and the products resulting from **4**, the stereochemical courses of the formation of **4** and its interception remain a matter of speculation, as to date **4** is not amenable to direct observation. The first question refers to the conversion of **1** into **4**: Which enantiomer of **4** preferentially emerges from (–)-**1**, (*P*)-**4** or (*M*)-**4**? In other words, which of the two hydrogen atoms, 1a-H or 6b-H, of (–)-**1** changes sides of the ring system more readily than the other? As illustrated in Scheme 3, we prefer 1a-H, because it has to only move past a hydrogen atom of the methylene group (C-2). On the other hand, 6b-H faces considerably more steric hindrance, as the adjacent carbon atom (C-6a) does not carry a hydrogen atom but a CH group. Consequently, (*P*)-**4** should be the major (ca. 70%) and (*M*)-**4** the minor species (ca. 30%) formed on treatment of (–)-**1**, dissolved in furans, with methyllithium.

Given this assignment and the experimentally based conclusion (see section 1) that (*P*)- and (*M*)-**4** do not interconvert under the reaction conditions, it has to be rationalised why (*P*)-**4** and (*M*)-**4** add to a furan to give exclusively **6** and *ent*-**6**, respectively, and not vice versa. Quantum chemical calculations[30] as well as the experimental result of the addition of (*Z*,*Z*)-1,4-dideuterio-1,3-butadiene to 1,2-cyclohexadiene[3] support a two-step mechanism via diradical intermediates not only for [2+2] but also for [4+2] cycloadditions of allenes. In addition, the interception of *rac*-**4** by 2-*tert*-butyl-5-methylfuran to give *rac*-**6b**, *rac*-**8**, and **9** in the ratio of 5:1:2 is inconsistent with a concerted process. Such a mechanism would demand bond making between the central allene carbon atom of **4**, which is the sterically least encumbered one, and the *tert*-butyl-substituted carbon atom of the furan, with formation of **9** as the major product. However, in the case of a diradical intermediate (see **13**, Scheme 5), this should preferentially emerge from the attack of the central allene carbon atom of **4** at the methyl-bearing carbon atom of the furan, which is the easier accessible of the two reaction centres.

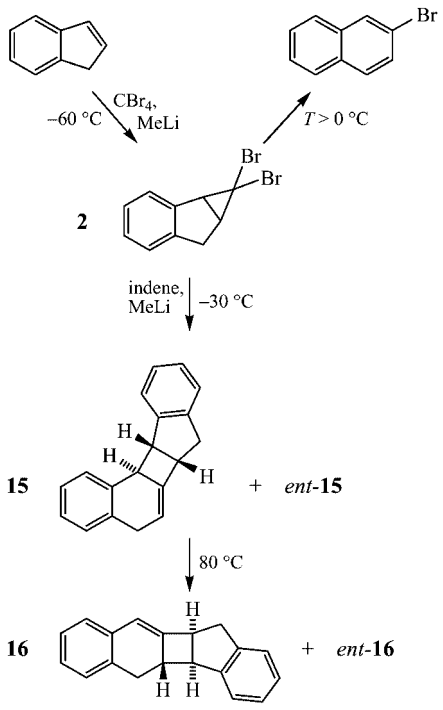


Scheme 5. Possible transition states (**12**, **14**) for the addition of the central allene carbon atom of (*P*)- and (*M*)-**4** to one of the enantiotopic faces of the CR^1 group of a furan of Scheme 3, with formation of the diradical **13**, being the intermediate en route to **6**. The enantiomers (*P*)-**4** (**12**) and (*M*)-**4** (**14**) are represented by the CH=C=CH subunits only and approach the furan from above the drawing plane.

Scheme 5 shows the diastereomeric transition states **12** and **14** for the formation of the diradicals **13** by addition of the central allene carbon atom of (*P*)-**4** (**12**) and (*M*)-**4** (**14**) to one of the enantiotopic faces of the CR^1 group of the furans (*Si*-face for R^1 = Me, *Re*-face for R^1 = *t*Bu). We consider **12** for the most favourable arrangement leading to **13** and eventually to **6**. The attack of (*M*)-**4** on the same face (**14**) would also give rise to **13**, but **14** is believed to suffer from overcrowding more than **12**. In both **12** and **14**, one hydrogen atom of the allene subunit interacts with R^1 about the same extent. However, the second hydrogen atom approaches the oxygen atom of the furan in **12** and the CH group of the 3-position in **14**. As the spatial demand of an oxygen atom is substantially smaller than that of a CH group, **12** should be preferred over **14**. Because our experiments suggest that (*P*)-**4** and (*M*)-**4** react most selectively to furnish **6** and *ent*-**6**, respectively (see Scheme 3), **14** seems to have no importance at all, and (*M*)-**4** adds to the other face of the CR^1 group of a furan via a transition state that is the mirror image of **12** (= *ent*-**12**) and leads to *ent*-**13** and eventually *ent*-**6**.

4. Trapping of Isonaphthalene 4 by Indene

The above furans undergo a [4+2] cycloaddition with isonaphthalene **4**, but [2+2] cycloadditions of **4** are not less common,[3,10,11] which is why we tested the stereochemical course of such a reaction as well. We tried out indene as a trapping reagent for **4**, which has been utilised to intercept only two six-membered cyclic allenes heretofore.[31] Indeed, the pentacyclic hydrocarbon *rac*-**15** (Scheme 6) was formed smoothly as the sole product.



Scheme 6. Preparation of the dibromocarbene adduct **2** of indene, its use as precursor of the isonaphthalene **4** within the one-pot procedure for the synthesis of the indene adduct *rac*-**15** of **4**, and the thermal rearrangement of *rac*-**15** to *rac*-**16**.

Being particularly simple, the one-pot procedure was employed for the preparation of *rac*-**15**. This method was briefly mentioned previously,[3,10] and takes advantage of the dibromocarbene adduct **2** of indene. An earlier attempt to obtain **2** under the routine conditions for the addition of dibromocarbene onto olefins ($HCBr_3$, KO*t*Bu) resulted in the formation of 2-bromonaphthalene.[32] The reasons for the instability of **2** are the same as those suggested for the conversion of **5** into 2-fluoronaphthalene (Scheme 2). In contrast to that of **5**, the existence of **2** could be proved directly by NMR spectroscopy. With this end in view, we treated a mixture of indene and tetrabromomethane with methyllithium[33] at –60 °C, then removed most of the solvent (diethyl ether) under reduced pressure at –60 °C, and recorded a ^{1}H NMR spectrum at –60 °C, which clearly indicated the presence of **2** (Scheme 6) by comparison with the ^{1}H NMR spectroscopic data of **1**. ^{1}H NMR spectra taken at –30 °C and 0 °C were unchanged relative to that obtained at –60 °C. However, the NMR sample darkened quickly at temperatures above 0 °C, and a spectrum recorded at 25 °C illustrated the decomposition of **2**, which most probably gave rise to 2-bromonaphthalene, although we did not prove that.

In order to synthesise *rac*-**15**, we treated **2**, which was obtained as detailed above at –60 °C, with methyllithium in the presence of indene at –30 °C and isolated the product in 30% yield. The configuration as drawn in Scheme 6 was determined by X-ray crystal structure analysis (Figure 7). As expected on the basis of experience with the styrene adduct of **4**,[10] the thermal stability of *rac*-**15** turned out to be limited. Heating at 80 °C gave rise to the isomer *rac*-**16**, the configuration of which was also established by X-ray crystal structure analysis (Figure 8). The difference in the thermodynamic stability of *rac*-**15** and *rac*-**16** is probably caused by the position of the ethylene subunit, which is isolated in the former but conjugated with a benzene group in the latter. In analogy with the rearrangements discussed above (**6b**→**8** and **6c**,**10**→**11**), the pathway from **15** to **16** should involve the diradical **19** (see Scheme 7).

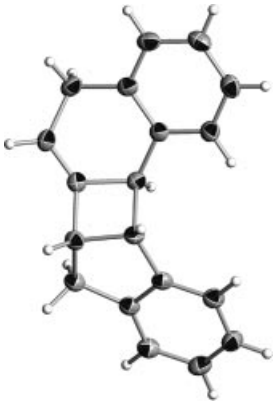


Figure 7. Molecular structure of **15**/*ent*-**15** as determined by X-ray crystal diffraction. The anisotropic displacement parameters are depicted at the 50% probability level.

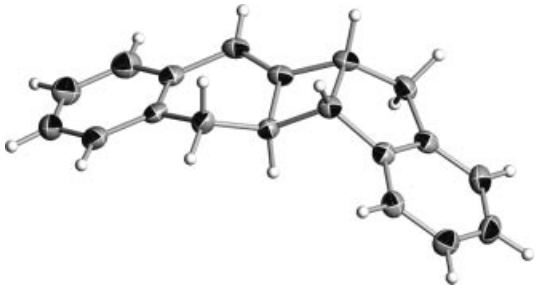
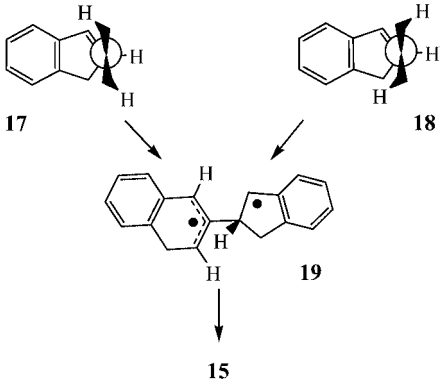


Figure 8. Molecular structure of **16**/*ent*-**16** as determined by X-ray crystal diffraction. The anisotropic displacement parameters are depicted at the 50% probability level.

Although we did not provide a large excess of indene for the interception of **4**, the 30% yield of *rac*-**15** indicated a relatively high reactivity of this allenophile towards **4**. By means of a competition experiment, indene and 2,5-dimethylfuran were shown to react equally fast.

By HPLC on Chiralcel OD, *rac*-**15** could be resolved. The absolute configuration was again established by comparison of the experimental and the calculated CD spectra



Scheme 7. Possible transition states (**17**, **18**) for the addition of the central allene carbon atom of (*P*)-**4** (**17**) and (*M*)-**4** (**18**) to the *Si*-face of indene en route to the diradical **19**, which is the precursor to **15**. The enantiomers **4** are represented by the CH=C=CH subunits only and approach indene from above the drawing plane.

(Figure 6), according to which the faster eluting compound is the enantiomer *ent*-**15**. When the pure enantiomers **1** were exposed to methyllithium in the presence of indene, the stereoselectivity was found to be lower than in the case of the above furans. The results are collated in Table 1.

Table 1. Ratios of enantiomers **15** and *ent*-**15** on trapping of **4** by indene, when **4** was generated from pure (+)- or (–)-**1** with methyllithium at –30 °C.

Substrate	Solvent	Ratio of **15**:*ent*-**15**
(+)-**1**	indene/diethyl ether, 1:1	52:48
(–)-**1**	indene/diethyl ether, 2:1	48:52
(–)-**1**	indene/THF, 2:2.8	42:58

Two reasons can be suggested to explain the lower stereoselectivity compared to that of the reactions of the furans above. One is the change of the solvent polarity and the other the small difference in the steric interaction of one enantiomer **4** with the enantiotopic faces of indene. Because of the solidification of indene at –2 °C, it could not be utilised in pure form as a reaction medium, but had to be diluted. Diethyl ether served this purpose, as some of it was anyway introduced as the solvent of methyllithium. As the first two entries of Table 1 show, the variation of the proportion of diethyl ether had no effect. Presumably, the mixtures of indene and diethyl ether employed were less polar than the pure furans in the above experiments. This might have influenced the conversion of an enantiomer **1** into (*P*)- and (*M*)-**4** in such a way so that almost equal amounts emerged. It is conceivable that this reaction is subject to a solvent effect, as the intermediate carbenoid, resulting from **1** and transforming to the carbene being the precursor to (*P*)- and (*M*)-**4**, is a highly polar molecule. Consistent with this explanation, the replacement of diethyl ether by THF, which in general solvates organolithium compounds better than diethyl ether does, resulted in an increase in the enantioselectivity (third entry in Table 1), and this may be traced back to an increased ratio of the enantiomers **4** on conversion of (–)-**1**.

The other possible origin for the low stereoselectivity resides in the similar size of the 1-CH_2 group and the 3-CH group of indene. Therefore, the transition states **17** and **18** (Scheme 7) for the attack of both enantiomers **4** to the *Si*-face of indene could be very close in energy. The result would be the diradical **19** and eventually **15**, whereas their enantiomers *ent*-**19** and *ent*-**15** would emerge from the addition of the enantiomers **4** to the *Re*-face of indene.

Conclusions

Firstly, the results of this work prove that the six-membered cyclic allene **4** is a chiral molecule. In addition, the experiments and the calculated CD spectra of several compounds enabled us to propose a model for the detailed stereochemical course of the generation of the enantiomers **4** from a pure enantiomer **1** in a Doering–Moore–Skattebøl reaction and the interception of **4** by 2,5-disubstituted furans. Accordingly, the partial loss of the stereochemical information introduced by a pure enantiomer **1** occurs in the first step, which provides a 70:30 mixture of (*P*)- and (*M*)-**4** from (–)-**1**. The interconversion of (*P*)- and (*M*)-**4**, previously calculated to have a barrier of only 11 kcal mol^{-1},[5] does not take place under the reaction conditions, because trapping by the furans proceeds much faster. As the product ratios **6**:*ent*-**6** are virtually independent of the spatial demand of the furans, we believe that the addition of an enantiomer **4** is highly stereoselective. More speculations are necessary to explain the facts in the case of indene as an important component of the solvent and as a reaction partner of **4**. The very low stereoselectivity, i.e. the almost equal amounts of **15** and *ent*-**15**, has its origin either in similar reaction rates for the formation of both enantiomers **4** from one enantiomer **1** due to a different solvent effect, as compared to the furans as solvent, or in the insignificant preference of one enantiomer **4** for one of the enantiotopic faces of indene.

To test these hypotheses and, if applicable, develop them further, the enantioselective generation of a 1-substituted 1,2-cyclohexadiene will be helpful, which is why we are currently investigating 1-phenyl-1,2-cyclohexadiene.

Experimental Section

General Remarks: NMR: Bruker Avance 400 and DMX 600 spectrometers; chemical shifts δ in ppm relative to Me_4Si (= 0 ppm) by using solvent signals as internal reference [$CDCl_3$: δ = 7.26 ppm (^{1}H NMR) and 77.0 ppm (^{13}C NMR); C_6D_6: δ = 7.16 ppm (^{1}H NMR of C_6D_5H) and 128.0 ppm (^{13}C NMR)]. MS: Finnigan MAT 8200 and MAT 90. Elemental analyses: Carlo Erba Strumentatione Elemental Analyser 1106. Melting points: Kofler hot stage apparatus from C. Reichert, Optische Werke AG, Vienna, Austria. UV: JASCO V-570 UV/Vis/NIR Spectrophotometer. CD: JASCO J-715 Spectropolarimeter. Specific rotations: JASCO P-1020 Polarimeter. Frequently used solvents: DEE = diethyl ether, PE = light petroleum ether (b.p. 40–65 °C), MTBE = *tert*-butyl methyl ether.

Resolution of Racemates and Analyses of Nonracemic Mixtures of Enantiomers: An HPLC system was used consisting of a Knauer

HPLC Pump 64, a Gynkotek UV-Detektor UVD, operated at 260 nm in most cases, and a Chiralcel OD column (250 × 21 mm), protected by a guard column (50 × 21 mm) with the same stationary phase. The flow rate of the eluants was maintained at 12 mL min^{-1}. Before use as eluants, the solvents were distilled from a Vigreux column (20 cm). During the chromatography, a constant stream of helium was bubbled through the solvents. The quantitative analysis of the UV signals was achieved with a Shimadzu C-R3A Chromatopac Integrator.

(1α,1aα,6bα)-1-Bromo-1-fluoro-1,1a,2,6b-tetrahydrocyclopropa[*a*]indene (*rac*-1): A solution of indene (23.2 g, 200 mmol), benzyltriethylammonium chloride (800 mg, 3.51 mmol), and dibromofluoromethane[34] (38.2 g, 199 mmol) in dichloromethane (100 mL) was cooled in an ice bath. After the addition of aqueous sodium hydroxide (32 g, 800 mmol in 32 mL of water), which was precooled to 5 °C, the mixture was intensively stirred for 3 d. During that period, it reached room temperature after several hours. Water (50 mL) was admixed, and the layers were separated. The aqueous phase was extracted with DEE (3 × 30 mL), the combined organic layers were dried with $MgSO_4$, and the solvents were evaporated in vacuo. Unreacted indene and 2-fluoronaphthalene, presumably formed via **5**, were removed by distillation at 65 °C (kugelrohr)/0.05 mbar. The remaining dark brown oil (9.6 g) was purified by flash chromatography (SiO_2; PE/MTBE, 40:1) to give *rac*-**1** (6.90 g, 15%) as a slightly brown solid, m.p. 71–72 °C (from methanol), which sublimed slowly at 20 °C/1 bar. ^{1}H NMR ($CDCl_3$): see ref.[10] ^{1}H NMR (400 MHz, C_6D_6): δ = 2.01 (tt, average of $J_{1a,2\alpha}$ and $J_{1a,6b}$ = 7.5, average of $J_{1a,2\beta}$ and $J_{1a,F}$ = 1.5 Hz, 1 H, 1a-H), 2.63 (br. dd, $J_{2\alpha,2\beta}$ = 17.6, $J_{1a,2\alpha}$ = 7.3 Hz, 1 H, 2-H$^{\alpha}$), 2.84 (br. d, $J_{2\alpha,2\beta}$ = 17.6 Hz, 1 H, 2-H$^{\beta}$), 2.85 (dd, $J_{1a,6b}$ = 7.7, $J_{6b,F}$ = 1.4 Hz, 1 H, 6b-H), 6.82 (m, 1 H, 3-H or 6-H), 6.91–6.99 (m, 2 H, 4-H, 5-H), 7.01 (m, 1 H, 6-H or 3-H) ppm. ^{13}C NMR: see ref.[10] UV (methanol): λ_{max} (log ε) = 276 (3.22), 270 (3.09), 262 (sh, 2.94), 230 (3.74), 215 (sh, 3.92) nm. MS (70 eV, EI): *m*/*z* (%) = 228, 226 (0.3%, 0.3%) $[M]^+$, 148 (11), 147 (100), 146 (44), 127 (18). $C_{10}H_8BrF$ (227.1): calcd. C 52.89, H 3.55; found: C 52.73, H 3.66.

Thermolysis of *rac*-1: Without a solvent, *rac*-**1** (100 mg, 0.44 mmol) was heated at 130 °C for 3.5 h. On cooling to room temperature, the product became a brown solid, which was recrystallised from ethanol to give 86 mg (94%) of 2-bromonaphthalene. Its identity was established by comparison of its ^{1}H NMR spectrum with that of an authentic sample.

Resolution of *rac*-1 and Determination of the Absolute Configuration of the Enantiomers: The equipment described above was used, and the elution was carried out with hexane/2-propanol, 199:1. Samples (100 μL) of a saturated solution of *rac*-**1** in 2-propanol were injected. The retention times were 9.5 min for (+)-**1** and 12 min for (–)-**1**. Per injection, 4.3 mg of each enantiomer were obtained. Specific rotation (methanol, *c* = 0.2, *T* = 20.8 °C): $[\alpha]_D$ = +62.1 and –61.5. CD (methanol): see Figure 3. The pure enantiomers are colourless solids with m.p. 70–71 °C. A single-crystal X-ray crystal structure determination established the 1*S*,1a*R*,6b*R*-configuration of (+)-**1** (Figure 1).

(1α,4α,4aα)-1,4,4a,9-Tetrahydro-1,4-dimethyl-1,4-epoxyphenanthrene (*rac*-6a): Under nitrogen, a stirred solution of *rac*-**1** (1.00 g, 4.40 mmol) in 2,5-dimethylfuran (20 mL) was cooled to –30 °C and was treated dropwise with methyllithium (16.5 mmol, 15 mL of 1.1 M in DEE) in a manner so that the temperature remained at –30 °C (30 min). After removal of the cooling bath, the temperature was allowed to rise to 0 °C, and the mixture was then cautiously hydrolysed (20 mL). The layers were separated, the aqueous layer was extracted with DEE (3 × 10 mL), and the combined organic phases were dried with $MgSO_4$ and concentrated in vacuo. The residue (1.2 g of a brown oil) was purified by flash chromatography (SiO_2; PE/MTBE, 20:1) to give *rac*-**6a** (390 mg, 40%) as a yellow oil, the spectroscopic data of which agreed with those reported previously.[11]

1,4-Dihydro-1,4-dimethyl-1,4-epoxyphenanthrene (*rac*-7): A mixture of *rac*-**6a** (390 mg, 1.74 mmol) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (500 mg, 2.20 mmol) in benzene (20 mL) was stirred at room temperature for 12 h. Then, pentane (20 mL) was added, the resulting precipitate was filtered off, the filtrate was concentrated in vacuo, and the residue, an orange oil, was purified by flash chromatography (SiO_2; pentane/DEE, 15:1) to give *rac*-**7** (242 mg, 63%) as a yellow oil, whose ^{1}H NMR spectrum agreed with the literature data.[35] UV (methanol): λ_{max} (log ε) = 336 (3.21), 308 (3.43), 264 (sh, 3.60), 254 (sh, 3.92), 246 (sh, 4.05), 229 (4.56) nm.

Resolution of *rac*-7: The equipment described above was used, and the elution was carried out with hexane/2-propanol, 99:1. Samples (100 μL) of a 0.2 M solution of *rac*-**7** in 2-propanol were injected. The retention times were 13.5 min for the (–)-enantiomer (**7**) and 17.5 min for the (+)-enantiomer (*ent*-**7**). Specific rotation (methanol, *c* = 0.1, *T* = 21 °C): $[\alpha]_D$ = +143 and –138. CD (methanol): see Figure 4.

Reaction of the Pure Enantiomers (+)- and (–)-1 with Methyllithium in the Presence of 2,5-Dimethylfuran and Subsequent Aromatisation of the Product: The reaction of (+)-**1** (100 mg, 0.440 mmol) with methyllithium (2.0 mmol, 2.0 mL of 1.0 M in DEE) in the presence of 2,5-dimethylfuran (4 mL) was conducted as described above for *rac*-**1**. Without purification, the crude product (160 mg) was dissolved in benzene (6 mL) and then dehydrogenated with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (140 mg, 0.616 mmol) as described above for *rac*-**6a**. The product was purified by chromatography (SiO_2; pentane/DEE, 10:1) to give a yellow oil (26 mg, 27%), which was shown to consist of **7** and *ent*-**7** in the ratio of 28:72. The structure of the product was confirmed by ^{1}H NMR spectroscopy, whereas the enantiomeric ratio was determined by HPLC analysis by applying the conditions as for the resolution of *rac*-**7**.

When (–)-**1** was used instead of (+)-**1**, the ratio of **7** and *ent*-**7** turned out to be 73:27.

In two further experiments, the enantiomers of **1** were not dissolved in pure 2,5-dimethylfuran prior to treatment with methyllithium, but in mixtures of 2,5-dimethylfuran with DEE. These mixtures were prepared by combining 3 and 2 mL of 2,5-dimethylfuran with 1 and 2 mL, respectively, of DEE to give a total volume of about 4 mL in each case. However, the ratios of **7** and *ent*-**7** were virtually the same as above, namely 72.5:27.5 from (–)-**1** and 27:73 from (+)-**1**.

In addition, one experiment was conducted at room temperature, whereas the ones above proceeded at –30 °C. Again, the ratio of **7** and *ent*-**7** turned out to be 72:28 from (–)-**1**.

(1α,4α,4aα)-4-*tert*-Butyl-1,4,4a,9-tetrahydro-1-methyl-1,4-epoxyphenanthrene (*rac*-6b), (1α,4α,4aα)-4-*tert*-Butyl-1,4,4a,10-tetrahydro-1-methyl-1,4-epoxyanthracene (*rac*-8), and (1α,4α,4aα)-1-*tert*-Butyl-1,4,4a,9-tetrahydro-4-methyl-1,4-epoxyphenanthrene (9): Under nitrogen, a stirred solution of *rac*-**1** (800 mg, 3.52 mmol) in 2-*tert*-butyl-5-methylfuran[36] (5 mL), cooled to –30 °C, was treated dropwise with methyllithium (5.50 mmol, 5 mL of 1.1 M in DEE) in a manner so that the temperature remained at –30 °C. After removal of the cooling bath, the temperature was allowed to rise to 0 °C, and the mixture was then cautiously hydrolysed (6 mL). The layers were separated, the aqueous layer was extracted with

DEE (3 × 5 mL), and the combined organic phases were dried with $MgSO_4$ and concentrated in vacuo (15 mbar). The residue still contained 2-*tert*-butyl-5-methylfuran, which was distilled off in a kugelrohr (40 °C/0.05 mbar) and thus recovered. The remaining product, 859 mg of an orange oil, was shown by NMR spectroscopy to contain *rac*-**6b**, *rac*-**8**, and **9** in the ratio of 5:1:2. Flash chromatography (SiO_2; PE/MTBE, 30:1) furnished an 8:1:2 mixture of *rac*-**6**, *rac*-**8**, and **9** as a light yellow oil (238 mg, 25%). MS (70 eV, EI): *m*/*z* (%) = 266 (8) $[M]^+$, 210 (13), 209 (20), 182 (15), 181 (100), 167 (18), 166 (30), 165 (32), 148 (28), 147 (38), 146 (20), 142 (11), 141 (13), 128 (20), 127 (18), 115 (25), 57 (21), 43 (23), 41 (10). HRMS (70 eV, EI): calcd. for $C_{19}H_{22}O$ $[M]^+$ 266.1665; found 266.1666.

***rac*-6b:** ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.32 (s, 9 H, *t*Bu), 1.68 (s, 3 H, 1-Me), 3.31–3.37 (m, 3 H, 9-H_2, 4a-H), 5.79 (m, 1 H, 10-H), 5.91 (d, $J_{2,3}$ = 5.6 Hz, 1 H, 2-H), 6.51 (d, $J_{2,3}$ = 5.6 Hz, 1 H, 3-H), 7.11–7.23 (m, 3 H, 6-H, 7-H, 8-H), 7.36 (dm, $J_{5,6} \approx 7$ Hz, 1 H, 5-H) ppm; the position of the substituents and the configuration is supported by a NOESY spectrum. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 15.6 (1-Me), 28.0 (*t*Bu-Me), 33.2 (C-9), 33.5 (*t*Bu-C_q), 49.2 (C-4a), 83.9 (C-1), 97.4 (C-4), 112.0 (C-10), 124.6 (C-5), 124.9, 125.0, 126.6 (C-6, C-7, C-8), 134.6 (C-3), 136.7 (C-2), 140.8, 140.9 (C-4b, C-8a), 150.4 (C-10a) ppm; as far as specified, the assignments are based on HMQC and HMBC spectra.

***rac*-8:** See next experiment.

9: ^{1}H NMR (600 MHz, C_6D_6; values in brackets refer to $CDCl_3$ as solvent): δ = 1.24 [1.21] (s, 9 H, *t*Bu), 1.83 [2.03] (s, 3 H, 4-Me), 3.02 [3.18] (dd, $J_{9\alpha,9\beta}$ = 17.6, $J_{9\beta,10}$ = 6.6 Hz, 1 H, 9-H^β), 3.08 [3.14] (dm, $J_{4a,9\alpha}$ = 6.2 Hz, 1 H, 4a-H), 3.14 [3.32] (br. d, $J_{9\alpha,9\beta}$ = 17.6, $J_{4a,9\alpha}$ = 6.2 Hz, 1 H, 9-H^α), 5.74 [5.96] (dt, $J_{9\beta,10}$ = 6.6, $J_{4a,10}$ = $J_{9\alpha,10}$ = 2.3 Hz, 1 H, 10-H), 5.93 [6.16] (d, $J_{2,3}$ = 5.6 Hz, 1 H, 3-H), 5.99 [6.26] (br. d, $J_{2,3}$ = 5.6 Hz, 1 H, 2-H), [7.28] (br. d, $J_{5,6} \approx$ 7.7 Hz, 1 H, 5-H) ppm; the signals of the other aromatic protons are superimposed by signals of *rac*-**6b** and *rac*-**8**. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 20.3 (4-Me), 26.5 (*t*Bu-Me), 32.5 (*t*Bu-C_q), 32.6 (C-9), 52.7 (C-4a), 86.1 (C-4), 95.5 (C-1), 114.0 (C-10), 122.9 (C-5), 125.6, 125.7, 126.8 (C-6, C-7, C-8), 135.5 (C-3), 136.1 (C-2), 138.3, 139.1, 145.8 (C-4b, C-8a, C-10a) ppm.

(1α,4α,4aα)-4-*tert*-Butyl-1,4,4a,10-tetrahydro-1-methyl-1,4-epoxyanthracene (*rac*-8) by Thermal Rearrangement of *rac*-6b: A solution of an 8:1:2 mixture of *rac*-**6b**, ***rac*-8**, and **9** (200 mg) in toluene (20 mL) was refluxed for 3 h. After evaporation of the solvent in vacuo (0.1 mbar), an NMR spectrum of the residue (193 mg) indicated that *rac*-**6b** had been converted completely into *rac*-**8**, whereas **9** had remained largely unchanged. Flash chromatography (SiO_2; PE/ethyl acetate, 33:1) furnished a 10:1 mixture of *rac*-**8** and **9** (136 mg, 68%) as a colourless oil. UV (methanol): λ_{max} (log ε) = 297 (sh, 3.67), 278 (3.95), 227 (sh, 4.19), 220 (4.32), 215 (4.32), 211 (sh, 4.29) nm. MS (70 eV, EI): *m*/*z* (%) = 266 (17) $[M]^+$, 223 (20), 209 (19), 194 (10), 182 (17), 181 (100), 167 (34), 166 (24), 165 (27), 57 (24), 43 (17). HRMS (70 eV, EI): calcd. for $C_{19}H_{22}O$ $[M]^+$ 266.1665; found 266.1666.

***rac*-8:** ^{1}H NMR (600 MHz, C_6D_6; the values in brackets refer to $CDCl_3$ as solvent): δ = 1.10 [1.19] (s, 9 H, *t*Bu), 1.52 [1.66] (s, 3 H, 1-Me), 2.33 [2.43] (br. dd, $J_{4a,10\beta}$ = 15.9, $J_{10\alpha,10\beta}$ = 14.5 Hz, 1 H, 10-H^β), 2.75 [2.94] (dd, $J_{10\alpha,10\beta}$ = 14.5, $J_{4a,10\alpha}$ = 5.8 Hz, 1 H, 10-H^α), 3.21 [3.20] (ddd, $J_{4a,10\beta}$ = 15.9, $J_{4a,10\alpha}$ = 5.8, $J_{4a,9}$ = 2.4 Hz, 1 H, 9-H), 5.90 [6.21] (d, $J_{2,3}$ = 5.6 Hz, 1 H, 3-H), 6.05 [6.19] (d, $J_{4a,9}$ = 2.4 Hz, 1 H, 9-H), 6.21 [6.47] (dd, $J_{2,3}$ = 5.6, J = 0.5 Hz, 1 H, 2-H), 6.89 [7.02] (dtq, $J_{5,6}$ = 7.3, further line distances 1.4, 0.7 Hz, 1 H, 5-H), 6.96 [7.02] (br. dd, $J_{7,8}$ = 7.3, $J_{6,8}$ = 1.4 Hz, 1 H, 8-H), 7.00 [7.07] (td, average of $J_{5,6}$ and $J_{6,7}$ = 7.4, $J_{6,8}$ = 1.4 Hz, 1 H, 6-H), 7.07 [7.13] (tt, average of $J_{6,7}$ and $J_{7,8}$ = 7.4, further line distance 1.1 Hz, 1 H, 7-H) ppm; the assignments are based on a NOESY spectrum. ^{13}C NMR (151 MHz, C_6D_6): δ = 14.8 (1-Me), 26.6 (*t*Bu-Me), 33.2 (*t*Bu-C_q), 35.7 (C-10), 43.4 (C-4a), 86.0 (C-1), 97.6 (C-4), 114.7 (C-9), 126.5 (C-8), 126.9 (C-6), 127.2 (C-7), 128.4 (C-5), 134.8 (C-10a), 135.2 (C-3), 135.6 (C-8a), 142.1 (C-2), 154.4 (C-9a) ppm; the assignments are based on HMQC and HMBC spectra.

Resolution of *rac*-8: The equipment described above was used, and the elution was carried out with hexane/2-propanol, 1000:1. Samples (100 μL) of an 0.1 M solution of *rac*-**8** in 2-propanol were injected. The retention times were 12.0 min for the (+)-enantiomer **8** and 13.5 min for the (–)-enantiomer (*ent*-**8**). Specific rotation (methanol, *c* = 0.5, *T* = 21 °C): $[\alpha]_D$ = +157 and –196. CD (methanol): see Figure 5.

Reaction of the Pure Enantiomer (+)-1 with Methyllithium in the Presence of 2-*tert*-Butyl-5-methylfuran and Subsequent Thermal Rearrangement of 6b/*ent*-6b to 8/*ent*-8: Under nitrogen, a stirred solution of (+)-**1** (130 mg, 0.572 mmol) in 2-*tert*-butyl-5-methylfuran (2 g), cooled to –30 °C, was treated dropwise with methyllithium (4.0 mmol, 5.0 mL of 0.8 M in DEE) in a manner so that the temperature remained at –30 °C. After removal of the cooling bath, the temperature was allowed to rise to 0 °C, and the mixture was then cautiously hydrolysed (5 mL). The layers were separated, the aqueous layer was extracted with DEE (3 × 5 mL), and the combined organic phases were dried with $MgSO_4$ and concentrated in vacuo. From the residue, the excess of 2-*tert*-butyl-5-methylfuran was distilled off in a kugelrohr (50 °C/15 mbar). The remaining oil (76 mg) was dissolved in toluene (10 mL), and the solution was refluxed for 4 h. The cold solution was concentrated in vacuo, and the residue was purified by flash chromatography (SiO_2; PE/ethyl acetate, 100:1) to furnish 8.4 mg (6%) of a colourless oil, which was shown to consist of **8** and *ent*-**8** in the ratio of 34:66 by HPLC on Chiralcel OD under the conditions described for the resolution of *rac*-**8**. The mixture was separated completely, and the solutions of **8** and *ent*-**8**, as obtained from HPLC, were concentrated in vacuo to a volume of 1 mL each. In one of the samples, crystals (m.p. 91–93 °C) formed on storage at –30 °C, which were subjected to X-ray crystal structure determination furnishing constitution and relative configuration, but not the absolute configuration of **8**/*ent*-**8** (Figure 2).

Relative Reactivity of 2,5-Dimethylfuran and 2-*tert*-Butyl-5-methylfuran Towards the Intermediate 4: Under nitrogen, a stirred solution of *rac*-**1** (50 mg, 0.22 mmol) in a mixture of 2,5-dimethylfuran (700 mg, 7.29 mmol) and 2-*tert*-butyl-5-methylfuran (1.00 g, 7.25 mmol) was treated with methyllithium (1.60 mmol, 2.0 mL of 0.8 M in DEE). The conditions and the workup were as described above for the analogous reaction of *rac*-**1** in one of the two furans as solvent. After the removal of the unreacted 2-*tert*-butyl-5-methylfuran by distillation in a kugelrohr (30 °C/0.02 mbar), the crude product (61 mg) was shown to contain *rac*-**6a**, *rac*-**6b**, *rac*-**8**, and **9** in the ratio of about 8:5:1:2 by NMR spectroscopy, indicating that 2,5-dimethylfuran and 2-*tert*-butyl-5-methylfuran trap **4** equally fast.

(1α,4α,4aα)-1,4-Bis(*tert*-butyl)-1,4,4a,9-tetrahydro-1,4-epoxyphenanthrene (*rac*-6c) and (1α,4α,4aα)-1,4-Bis(*tert*-butyl)-1,4,4a,10-tetrahydro-1,4-epoxyanthracene (*rac*-10): Under nitrogen, a stirred solution of *rac*-**1** (500 mg, 2.20 mmol) in 2,5-di-*tert*-butylfuran[37] (8 mL), cooled to –20 °C, was treated dropwise with methyllithium (10 mmol, 10 mL of 1.0 M in DEE) in a manner so that the temperature did not exceed –20 °C. After removal of the cooling bath, the temperature was allowed to rise to 0 °C, and the mixture was then cautiously hydrolysed (15 mL). The layers were separated, the

aqueous layer was extracted with DEE (3×10 mL), and the combined organic phases were dried with $MgSO_4$ and concentrated in vacuo. The unreacted 2,5-di-*tert*-butylfuran was distilled off usinf a kugelrohr (40 °C/0.05 mbar) and thus recovered. The residue (390 mg) was purified by flash chromatography (SiO_2; PE/ethyl acetate, 70:1) to give *rac*-**6c** and *rac*-**10** (69 mg, 10%) in the ratio of 5:1 as a colourless oil. MS (70 eV, EI): *m*/*z* (%) = 308 (4) $[M]^+$, 252 (36), 251 (28), 237 (16), 235 (10), 195 (19), 181 (11), 167 (27), 165 (12), 143 (11), 142 (13), 141 (10), 128 (14), 84 (29), 57 (100), 41 (17). HRMS (70 eV, EI): calcd. for $C_{22}H_{28}O$ $[M]^+$ 308.2135; found 308.2137. The UV spectrum virtually coincided with that of *rac*-**8** when superimposed, indicating that *rac*-**6c** has much lower molar extinction coefficients than *rac*-**10**. This should be particularly valid for the long-wave part of the spectrum, as *rac*-**6c** has only an isolated benzene chromophore, whereas *rac*-**10** is a styrene derivative. Indeed, the calculation of the UV spectrum of **6c** with the methods described in section 2 gave a result that significantly deviated from the experimental spectrum of the 5:1 mixture of *rac*-**6c** and *rac*-**10**.

***rac*-6c:** ^{1}H NMR (600 MHz, C_6D_6): δ = 1.20 (s, 9 H, 1-*t*Bu), 1.25 (s, 9 H, 4-*t*Bu), 3.05 (br. dd, $J_{9\alpha,9\beta}$ = 16.8, $J_{9\beta,10}$ = 6.4 Hz, 1 H, 9-H^β), 3.10 (ddd, $J_{9\alpha,9\beta}$ = 16.8, $J_{4a,9\alpha}$ = 4.7, $J_{9\alpha,10}$ = 2.3 Hz, 1 H, 9-H^α), 3.30 (m, 1 H, 4a-H), 5.77 (dt, $J_{9\beta,10}$ = 6.4, $J_{4a,10}$ = $J_{9\alpha,10}$ = 2.3 Hz, 1 H, 10-H), 5.83 (dd, $J_{2,3}$ = 5.7, J = 0.6 Hz, 1 H, 2-H), 6.29 (d, $J_{2,3}$ = 5.7 Hz, 1 H, 3-H), 7.03–7.07 (m, 2 H, 7-H, 8-H), 7.10 (m, 1 H, 6-H), 7.32 (br. d, $J_{5,6}$ = 7.6 Hz, 1 H, 5-H) ppm; the assignments are based on COSY and NOESY experiments. ^{13}C NMR (151 MHz, C_6D_6): δ = 26.5 (1-*t*Bu-Me), 28.0 (4-*t*Bu-Me), 32.8 (1-*t*Bu-C_q), 33.7 (C-9), 33.9 (4-*t*Bu-C_q), 51.3 (C-4a), 93.5 (C-1), 96.0 (C-4), 114.3 (C-10), 125.0 (C-5), 125.1 (double intensity, C-6, C-7), 126.5 (C-8), 133.5 (C-2), 135.1 (C-3), 140.8 (C-8a), 141.5 (C-4b), 147.7 (C-10a) ppm; the assignments are based on HSQC and HMBC spectra.

***rac*-10:** ^{1}H NMR (600 MHz, C_6D_6): δ = 1.07 (s, 9 H, 4-*t*Bu), 1.21 (s, 9 H, 1-*t*Bu), 2.32 (br. dd, $J_{10\alpha,10\beta}$ = 14.4, $J_{4a,10\beta}$ = 15.8 Hz, 1 H, 10-H^β), 2.73 (dd, $J_{10\alpha,10\beta}$ = 14.4, $J_{4a,10\alpha}$ = 5.7 Hz, 1 H, 10-H^α), 3.14 (ddd, $J_{4a,10\beta}$ = 15.8, $J_{4a,10\alpha}$ = 5.7, $J_{4a,9}$ = 2.4 Hz, 1 H, 4a-H), 5.91 (d, $J_{2,3}$ = 5.7 Hz, 1 H, 3-H), 6.41 (br. d, $J_{4a,9}$ = 2.4 Hz, 1 H, 9-H), 6.49 (dd, $J_{2,3}$ = 5.7, J = 0.6 Hz, 1 H, 2-H), 6.88 (br. d, $J_{5,6}$ = 7.3 Hz, 1 H, 5-H), 6.91 (br. dd, $J_{7,8}$ = 7.4, $J_{6,8}$ = 1.4 Hz, 1 H, 8-H), 7.00 (td, $J_{5,6}$ = $J_{6,7}$ = 7.4 Hz, $J_{6,8}$ = 1.4 Hz, 1 H, 6-H), ca. 7.50 (superimposed by signals of *rac*-**6c**, 7-H) ppm; the assignments are based on COSY and NOESY experiments. ^{13}C NMR (151 MHz, C_6D_6): δ = 26.6 (4-*t*Bu-Me), 26.7 (1-*t*Bu-Me), 32.8 (1-*t*Bu-C_q), 33.3 (4-*t*Bu-C_q), 35.4 (C-10), 44.9 (C-4a), 95.4 (C-1), 96.2 (C-4), 117.1 (C-9), 126.6 (C-8), 126.9 (C-6), 127.1 (C-7), 128.1 (C-5), 134.4 (C-10a), 135.5 (C-3), 135.8 (C-8a), 138.8 (C-2), 152.3 (C-9a) ppm; the assignments are based on HSQC and HMBC spectra.

Resolution of the Mixture of *rac*-6c and *rac*-10: The equipment described above was used, and the elution was carried out with hexane/2-propanol, 1000:1. As the 5:1 mixture of *rac*-**6c** and *rac*-**10** could not be separated by flash chromatography, samples (100 μL) of its 0.05 M solution in hexane were injected. Two signals of equal intensity were observed. The corresponding substances were collected separately and characterised by ^{1}H NMR spectroscopy showing that they still contained **6c**/*ent*-**6c** and **10**/*ent*-**10** in about the ratio of the racemates injected. However, the CD spectra were mirror images to each other and virtually coincided with those of **8** and *ent*-**8**, respectively, when superimposed. As our HPLC system operates with a UV detector, it shows the strongest response to compounds with a high molar absorptivity. Although **6c** and *ent*-**6c** were in excess, the signals came from **10** and *ent*-**10**. Owing to the similarity of the CD spectra with those of **8** and *ent*-**8**, the signal with a retention time of 8.3 min was assigned to *ent*-**10** and that at 9.3 min to **10**. Whether **6c** or *ent*-**6c** had the same retention time as **10** or *ent*-**10** could not be decided.

Reaction of the Pure Enantiomer (+)-1 with Methyllithium in the Presence of 2,5-Bis(*tert*-butyl)furan: Under nitrogen, a stirred solution of (+)-**1** (300 mg, 1.32 mmol) in 2,5-di-*tert*-butylfuran (6 mL), cooled to –25 °C, was treated dropwise with methyllithium (4.5 mmol, 5.0 mL of 0.9 M in DEE) in a manner so that the temperature remained at –25 °C. After removal of the cooling bath, the temperature was allowed to rise to 0 °C, and the mixture was then cautiously hydrolysed (5 mL). The layers were separated, the aqueous layer was extracted with DEE (3×5 mL), and the combined organic phases were dried with $MgSO_4$ and concentrated in vacuo (15 mbar). From the remaining oil, the excess of 2,5-di-*tert*-butylfuran was distilled off in a kugelrohr (40 °C/0.05 mbar). The residue was purified by flash chromatography (SiO_2; PE/ethyl acetate, 80:1) to furnish a mixture of **6c**, *ent*-**6c**, **10**, and *ent*-**10** (24 mg, 6%) as a colourless oil. The ratio of **10**:*ent*-**10** was determined to be 26:74 according to the procedure described for the resolution of *rac*-**6c**/*rac*-**10**. This ratio is also valid for **6c** and *ent*-**6c**, because **6c** and **10** emerge from a common diradical precursor (see **13** in Scheme 5) and *ent*-**6c** and *ent*-**10** from its enantiomer (*ent*-**13**).

Relative Reactivity of 2,5-Dimethyl- and 2,5-Bis(*tert*-butyl)furan Towards the Isonaphthalene 4: Under nitrogen, a stirred solution of *rac*-**1** (50 mg, 0.22 mmol) in a mixture of 2,5-dimethylfuran (1.35 g, 14.1 mmol) and 2,5-di-*tert*-butylfuran (2.53 g, 14.1 mmol) was treated with methyllithium (1.60 mmol, 2.0 mL of 0.8 M in DEE). The conditions and the workup were as described above for the analogous reactions of *rac*-**1** in one of the two furans as solvent. After removal of the unreacted 2,5-di-*tert*-butylfuran by distillation in a kugelrohr (30 °C/0.02 mbar), the crude product (48 mg) was shown to contain *rac*-**6a**, *rac*-**6c**, and **10** in a ratio of about 60:5:1 by NMR spectroscopy, indicating that 2,5-dimethylfuran traps **4** ten times as fast as 2,5-di-*tert*-butylfuran.

2,9b-Di-*tert*-butyl-3a,3b,4,9b-tetrahydronaphtho[2′,3′:3,4]cyclobuta-[1,2-*b*]furan (11): A solution of *rac*-**6c** and *rac*-**10** in the ratio of 5:1 (69 mg) in benzene (5 mL) was refluxed for 6 h. After evaporation of the solvent in vacuo, the residue was purified by flash chromatography (SiO_2; PE/ethyl acetate, 114:1) to give a colourless oil (16 mg, 23%), which was shown by NMR spectroscopy to consist mainly of **11**. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.06 (s, 9 H, 9b-*t*Bu), 1.12 (s, 9 H, 2-*t*Bu), 2.31 (br. dd, $J_{4,4}$ = 14.6, $J_{3b,4}$ = 7.7 Hz, 1 H) and 3.11 (tt, average of $J_{3b,4}$ and $J_{4,4}$ = 14.5, J = 1.0 Hz, 1 H) (4-H_2), 2.83 (dtd, $J_{3b,4}$ = 14.4, average of $J_{3b,4}$ and $J_{3a,3b}$ = 7.7, $J_{3b,9}$ = 2.7 Hz, 1 H, 3b-H), 3.31 (dd, $J_{3a,3b}$ = 7.8, $J_{3,3a}$ = 2.8 Hz, 1 H, 3a-H), 4.50 (d, $J_{3,3a}$ = 2.8 Hz, 1 H, 3-H), 6.49 (br. d, $J_{3b,9}$ = 2.7 Hz, 1 H, 9-H), 6.94 (m, 1 H), 6.95–7.05 (m, 3 H) ppm; as far as specified, the assignment is based on a HMBC spectrum. ^{13}C NMR (101 MHz, C_6D_6): δ = 24.5 (9b-*t*Bu-Me), 28.1 (2-*t*Bu-Me), 28.3 (C-4), 32.6 (2-*t*Bu-C_q), 34.2 (9b-*t*Bu-C_q), 40.2 (C-3b), 46.3 (C-3a), 90.9 (C-3), 99.7 (C-9b), 120.6 (C-9), 126.75, 126.84, 126.85, 128.7 (C-5, C-6, C-7, C-8), 135.4, 136.3 (C-4a, C-8a), 147.6 (C-9a), 169.3 (C-2) ppm; as far as specified, the assignment is based on HMBC and HMQC spectra.

(1a*α*,6b*α*)-1,1-Dibromo-1,1a,2,6b-tetrahydrocyclopropa[*a*]indene (2): Under nitrogen, a stirred solution of indene (500 mg, 4.30 mmol) and tetrabromomethane (1.57 g, 4.73 mmol) in anhydrous DEE (7 mL), cooled to –60 °C, was treated dropwise with methyllithium (4.80 mmol, 3.29 mL of 1.46 M in DEE) within 30 min. The resulting yellow solution was stirred for further 15 min at –60 °C and then concentrated in vacuo (0.01 mbar) at that temperature. To the residue, whose main component was DEE, $CDCl_3$ was added at

–60 °C, and ^{1}H NMR spectra were recorded at –60, –30, 0, and +25 °C, which indicated the presence of **2** in the first three cases. Up to 0 °C, the sample was yellow; it darkened rapidly above 0 °C. ^{1}H NMR at 0 °C: see ref.[10]

(5aα,11bβ,11cα)-5a,7,11b,11c-Tetrahydro-5*H*-indeno[2′,1′:3,4]cyclobuta[1,2-*a*]naphthalene (*rac*-15): Under nitrogen, a stirred solution of indene (4.00 g, 34.4 mmol) and tetrabromomethane (12.0 g, 36.2 mmol) in anhydrous DEE (20 mL), cooled to –60 °C, was treated dropwise with methyllithium (36 mmol, 36 mL of 1.0 M in DEE). The mixture was then allowed to warm to –30 °C within 30 min and treated dropwise with methyllithium (36 mmol, 36 mL of 1 M in DEE) at that temperature. After removal of the cooling bath, the temperature was allowed to rise to 0 °C, and the mixture was then cautiously hydrolysed (30 mL). The layers were separated, the aqueous layer was extracted with DEE (3 × 30 mL), and the combined organic phases were dried with $MgSO_4$ and concentrated in vacuo (15 mbar). From the remaining oil, the unreacted indene was distilled off in a kugelrohr (40 °C/0.02 mbar). The residue was purified by flash chromatography (SiO_2; pentane/DEE, 20:1) to give *rac*-**15** (1.26 g) as a light yellow oil. The yield was 30 and 14% with reference to indene and tetrabromomethane, respectively. When 2 equiv. of indene and 1 equiv. of tetrabromomethane were utilised, the yield was about 30% with reference to tetrabromomethane. MS (70 eV, EI): *m*/*z* (%) = 244 (34) $[M]^+$, 239 (11), 229 (37), 228 (29), 226 (11), 195 (10), 165 (10), 129 (22), 128 (100), 127 (14), 116 (91), 115 (49), 91 (13), 45 (23), 44 (12), 43 (13). HRMS (70 eV, EI): calcd. for $C_{19}H_{16}$ $[M]^+$ 244.1247; found 244.1248. UV (methanol): λ_{max} (logε) = 277 (3.40), 270 (3.39), 263 (sh, 3.29), 257 (sh, 3.21), 226 (sh, 4.14), 216 (sh, 4.33) nm. ^{1}H NMR (600 MHz, C_6D_6): δ = 3.02 (ddd, $J_{7,7}$ = 18.3, $J_{6,7}$ = 6.5, $J_{7,11b}$ = 2.2 Hz, 1 H) and 3.08 (ddm, $J_{7,7}$ = 18.3, $J_{7,11b}$ = 7.4 Hz, 1 H) (7-H_2), 3.11 (dd, $J_{5,5}$ = 16.9, $J_{5,5a}$ = 10.3 Hz, 1 H) and 3.17 (dd, $J_{5,5}$ = 16.9, $J_{5,5a}$ = 5.1 Hz, 1 H) (5-H_2), 3.48 (m, 1 H, 5a-H), 3.68 (m, 1 H, 11b-H), 3.79 (t-like, average of $J_{5a,11c}$ and $J_{11b,11c}$ = 6.2 Hz, 1 H, 11c-H), 5.59 (dddd, $J_{6,7}$ = 6.5, $J_{5a,6}$ and $J_{6,7}$ and $J_{6,11b}$ = 3.2, 2.3, 1.1 Hz, 1 H, 6-H), 7.03 (br. d, $J_{8,9}$ = 7.5 Hz, 1 H, 8-H), 7.09–7.16 (m, 4 H, 2-H, 3-H, 4-H, 9-H), 7.20 (br. t, $J_{9,10}$ = $J_{10,11}$ = 7.4 Hz, 1 H, 10-H), 7.23 (br. d, $J_{1,2}$ = 6.9 Hz, 1 H, 1-H), 7.33 (br. d, $J_{10,11}$ = 7.4 Hz, 1 H, 11-H) ppm; as far as specified, the assignments are based on a H,H-COSY spectrum. ^{13}C NMR (151 MHz, C_6D_6): δ = 31.1 (C-7), 37.6 (C-5), 45.5 (C-5a), 53.3 (C-11b), 53.8 (C-11c), 115.1 (C-6), 123.8 (C-1), 125.5, 126.2, 127.0, 127.1 (C-2, C-3, C-4, C-9), 125.9 (C-11), 126.3 (C-10), 128.4 (C-8), 137.2, 139.6, 145.5, 145.8, 146.9 (C-4a, C-5b, C-7a, C-11a, C-11d) ppm; as far as specified, the assignments are based on a HSQC spectrum.

Resolution of *rac*-15: The equipment described above was used, and the elution was carried out with hexane/2-propanol, 834:1. Samples (100 µL) of a 0.1 M solution of *rac*-**15** in hexane were injected. The retention times were 15.4 min for the (–)-enantiomer (*ent*-**15**) and 17.8 min for the (+)-enantiomer **15**. Specific rotation (hexane, *c* = 0.2, *T* = 21 °C): $[\alpha]_D$ = –40 and +37. CD (methanol): see Figure 6.

Reactions of the Pure Enantiomers (+)-1 and (–)-1 with Methyllithium in the Presence of Indene: Under nitrogen, a stirred solution of (+)-**1** (50 mg, 0.22 mmol) and indene (1.00 g, 8.61 mmol) in anhydrous DEE (1.0 mL), cooled to –30 °C, was treated dropwise with methyllithium (2.4 mmol, 3.0 mL of 0.8 M in DEE) in a manner so that the temperature remained at –30 °C (20 min). After removal of the cooling bath, the temperature was allowed to rise to 0 °C, and the mixture was then hydrolysed (3 mL). The layers were separated, the aqueous layer was extracted with DEE (3 × 5 mL), and the combined organic phases were dried with $MgSO_4$ and concentrated in vacuo (15 mbar). From the remaining oil, the excess of indene was distilled off in a kugelrohr (40 °C/0.04 mbar). The residue was purified by flash chromatography (SiO_2, PE/ethyl acetate, 51:1) to give a colourless oil (15 mg, 28%), which was shown to be a 52:48 mixture of **15** and *ent*-**15** by the procedure described for the resolution of *rac*-**15**.

When (–)-**1** (175 mg, 0.77 mmol), dissolved in a mixture of indene (3.00 g, 25.8 mmol) and DEE (1.5 mL), was treated with methyllithium as described above for (+)-**1**, the workup furnished **15** and *ent*-**15** (50 mg, 27%) in the ratio of 48:52.

When (–)-**1** (155 mg, 0.68 mmol), dissolved in a mixture of indene (2.00 g, 17.2 mmol) and anhydrous THF (2.8 mL), was treated with methyllithium as described above for (+)-**1**, the workup furnished **15** and *ent*-**15** (10 mg, 6%) in the ratio of 42:58. On storage of this mixture at 4 °C over several months, colourless needles formed, m.p. 82–84 °C, which were used for the X-ray crystal structure analysis (Figure 7).

Relative Reactivity of Indene and 2,5-Dimethylfuran Towards the Isonaphthalene 4: Under nitrogen, a stirred solution of *rac*-**1** (100 mg, 0.44 mmol) in a mixture of indene (1.21 g, 10.4 mmol) and 2,5-dimethylfuran (1.00 g, 10.4 mmol) was treated with methyllithium (1.60 mmol, 2.0 mL of 0.8 M in DEE). The conditions and the workup were as described for the analogous reaction of (+)- and (–)-**1** in indene/DEE. The crude product was a yellow oil (96 mg) and contained the cycloadducts **6a** and **15** in the ratio of 1:1. Thus, indene and 2,5-dimethylfuran trap **4** equally fast.

(5aα,11aβ,11bα)-5a,11,11a,11b-Tetrahydro-5*H*-indeno[2′,1′:3,4]cyclobuta[1,2-*b*]naphthalene (16): A solution of *rac*-**15** (676 mg, 2.77 mmol) in benzene (30 mL) was refluxed for 11 h. The solvent of the brown solution was then evaporated in vacuo, and the residue was purified by flash chromatography (SiO_2; PE/ethyl acetate, 41:1) to give *rac*-**16** (86 mg, 13%) as colourless solid, m.p. 80–82 °C. Crystals for the X-ray crystal structure analysis (Figure 8) were obtained by dissolution of the solid in hexane (1.5 mL) and storage of the solution at –30 °C. MS (70 eV, EI): *m*/*z* (%) = 244 (39) $[M]^+$, 239 (14), 229 (43), 228 (32), 226 (12), 129 (20), 128 (88), 117 (10), 116 (100), 115 (41), 114 (16), 113 (10), 101 (10), 91 (12). HRMS (70 eV, EI): calcd. for $C_{19}H_{16}$ $[M]^+$ 244.1247; found 244.1248. ^{1}H NMR (600 MHz, C_6D_6): δ = 2.55–2.75 (m, 3 H, 11-H_2, 11a-H), 3.07 (br. dd, $J_{5,5}$ = 17.0, $J_{5\beta,5a}$ = 5.2 Hz, 1 H, 5-H^β), 3.11 (dd, $J_{5,5}$ = 17.0, $J_{5\alpha,5a}$ = 10.2 Hz, 1 H, 5-H^α), 3.30 (m, 1 H, 11b-H), 3.60 (m, 1 H, 5a-H), 6.16 (br. s, 1 H, 6-H), 6.93–7.02 (m, 3 H), 7.04–7.12 (m, 5 H) ppm; as far as specified, the assignments are based on a H,H COSY spectrum. ^{13}C NMR (151 MHz, C_6D_6): δ = 34.3 (C-11), 37.9 (C-5), 45.5 (C-5a), 46.0 (C-11a), 51.1 (C-11b), 116.9 (C-6), 123.8 (C-1), 125.3 (C-4), 126.2 (C-7), 126.3, 126.8, 126.9, 127.0 (C-2, C-3, C-8, C-9), 128.4 (C-10), 135.3, 135.8 (C-6a, C-10a), 145.4, 146.7 (C-4a, C-11c), 147.1 (C-5b) ppm; as far as specified, the assignments are based on HSQC and HMBC spectra.

X-ray Crystal Structure Determinations of (+)-1, 8/*ent*-8, 15/*ent*-15, and 16/*ent*-16: The data for (+)-**1**, **8**/*ent*-**8**, and **16**/*ent*-**16** were collected from shock-cooled crystals on a Bruker Smart APEX diffractometer with a D8 goniometer (graphite-monochromated Mo-K_α radiation, λ = 71.073 pm) equipped with a low-temperature device operating at 193(2) K.[38] The data for **15**/*ent*-**15** were collected from shock-cooled crystals on a STOE IPDS II diffractometer (graphite-monochromated Mo-K_α radiation, λ = 71.073 pm) equipped with a low-temperature device operating at 133(2) K.[38] An empirical absorption correction with the program SADABS 2.10 was employed for all structures.[39] They were solved by direct methods (SHELXS-97[40]) and refined by full-matrix least-squares methods against F_2 (SHELXL-97[41]). *R* values: $R_1 = \Sigma||F_o|-|F_c||/$

$\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$, $P = 1/3[\max(F_o^2,0) + 2F_c^2]$.

(+)-1: $C_{10}H_8BrF$, M = 227.08, orthorhombic, space group $P2_12_12_1$, Z = 4, a = 505.80(4) pm, b = 983.77(8) pm, c = 1692.01(14) pm, V = 0.84193(12) nm^3, ρ_c = 1.791 Mg·m^{-3}, 7902 reflections measured, 1726 unique, R_1 [$I > 2\sigma(I)$] = 0.0149, wR_2 (all data) = 0.0382, g_1 = 0.0258, g_2 = 0.1754 for 141 parameters and 0 restraints, GooF = 1.058, residual density (max./min.) = 0.248/–0.257 e·Å^{-3}, Flack parameter = –0.003(8), absolute configuration determined.

8/*ent*-8: $C_{19}H_{22}O$, M = 266.38, monoclinic, space group $P2_1$, Z = 2, a = 739.79(7) pm, b = 940.54(8) pm, c = 1090.15(10) pm, β = 98.5930(10)°, V = 0.75001(12) nm^3, ρ_c = 1.179 Mg·m^{-3}, 16114 reflections measured, 3070 unique, R_1 [$I > 2\sigma(I)$] = 0.0329, wR_2 (all data) = 0.0863, g_1 = 0.0545, g_2 = 0.0934 for 269 parameters and 1 restraint, GooF = 1.072, residual density (max./min.) = 0.230/–0.176 e·Å^{-3}, Flack parameter = 0.3(11), absolute configuration could not be determined.

15/*ent*-15: $C_{19}H_{16}$, M = 244.34, monoclinic, space group $P2_1/n$, Z = 4, a = 1102.3(2) pm, b = 530.89(11) pm, c = 2227.4(5) pm, β = 97.05(3)°, V = 1.2936(5) nm^3, ρ_c = 1.254 Mg·m^{-3}, 7461 reflections measured, 2452 unique, R_1 [$I > 2\sigma(I)$] = 0.0338, wR_2 (all data) = 0.0867, g_1 = 0.0417, g_2 = 0.0338 for 184 parameters and 0 restraints, GooF = 1.039, residual density (max./min.) = 0.160/–0.135 e·Å^{-3}.

16/*ent*-16: $C_{19}H_{16}$, M = 244.34, monoclinic, space group $P2_1/c$, Z = 4, a = 2483.0(2) pm, b = 616.29(6) pm, c = 847.64(8) pm, β = 91.530(2)°, V = 1.2966(2) nm^3, ρ_c = 1.252 Mg·m^{-3}, 27579 reflections measured, 2657 unique, R_1 [$I > 2\sigma(I)$] = 0.0746, wR_2 (all data) = 0.1752, g_1 = 0.0330, g_2 = 2.3117 for 221 parameters and 0 restraints, GooF = 1.230, residual density (max./min.) = 0.299/–0.235 e·Å^{-3}.

All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms of (+)-**1** and **8**/*ent*-**8** as well as the bridgehead hydrogen atoms of **15**/*ent*-**15** were located by difference Fourier syntheses and refined isotropically, whilst those of **16**/*ent*-**16** and the nonbridgehead hydrogen atoms of **15**/*ent*-**15** were assigned ideal positions and refined isotropically by using a riding model with U_{iso} constrained to 1.2 times the U_{eq} of the parent atom. Compound **16**/*ent*-**16** crystallised as a nonmerohedral twin. Therefore, two matrices for the two twin domaines have been determined by using the program GEMINI.[42] The data were then integrated by using the integration software SAINT[43] and the orientation matrix of the main twin domain. The twin rotation matrix was determined from the integrated data with the program ROTAX implemented in the program suite WinGX.[44] Based on the 180° rotation twin axis, a HKLF5 file was received (2 BASF parameters), which was used for the subsequent refinements. This procedure led to a sophisticated structural model with drastically reduced R values compared to a standard refinement omitting the twinning.

CCDC-607798, -607799, -607800, and -607801 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Cartesian coordinates and absolute energies of the compounds (+)-**1**, (–)-**1**, **7**, *ent*-**8**, and *ent*-**15**.

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