DOI: 10.1002/chem.200801355

9,10-Diarylanthracenes as Molecular Switches: Syntheses, Properties, Isomerisations and Their Reactions with Singlet Oxygen

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Abstract: A series of 9,10-diarylanthracenes with various substituents at the *ortho* positions have been synthesised by palladium-catalysed cross-coupling reactions. Such compounds exhibit interesting physical properties and can be applied as molecular switches. Despite the high steric demand of the substituents, products were formed in moderate-to-good yields. In some cases, microwave conditions further improved yields. Bis-coupling afforded two isomers (*syn* and *anti*) that do not interconvert at room temperature. These products were easily separated and their relative stereochemistries were unequivocally assigned by NMR spectroscopy and X-ray analysis. The *syn* and *anti* isomers exhibit different physical properties (e.g., melting points and solubilities) and interconversion by rotation around the aryl–aryl axis commences at $<100\,^{\circ}C$ for fluoro-substituted diarylanthracenes and at $>300\,^{\circ}C$ for alkyl- or alkoxy-substituted diarylanthracenes. The reactions with singlet oxygen were studied separately and revealed different reactivities and reaction pathways. The yields and reactivities depend on the size and electronic nature of the substituents. The *anti* isomers form the same 9,10-endoperoxides as the *syn* species, occasionally accompanied by unexpected 1,4-endoperoxides as byproducts. Thermolysis of the endoperoxides exclusively yielded the *syn* isomers. The interesting rotation around the aryl–aryl axis allows the application of 9,10-diarylanthracenes as molecular switches, which are triggered by light and air under mild conditions. Finally, the oxygenation and thermolysis sequence provides a simple, synthetic access to a single stereoisomer (*syn*) from an unselective coupling step.

Keywords: acenes · anthracene · isomerization · molecular devices · oxidation

Introduction

Polyaromatic hydrocarbons have received growing interest in materials science owing to their importance as components of electronic and photonic devices.[1] Anthracene is the smallest member of this class that has been proven to act as an organic field-effect transistor (OFET) and an organic light-emitting diode (OLED).[2] Some aryl derivatives of anthracene also benefit from the reversible addition of singlet oxygen ($^1O_2$) to the centre ring,[3] which, in general, makes them suitable as photochromic materials and as photoresists for lithography.[4] Consequently, chemists have focused on new syntheses of substituted arylanthracene derivatives.

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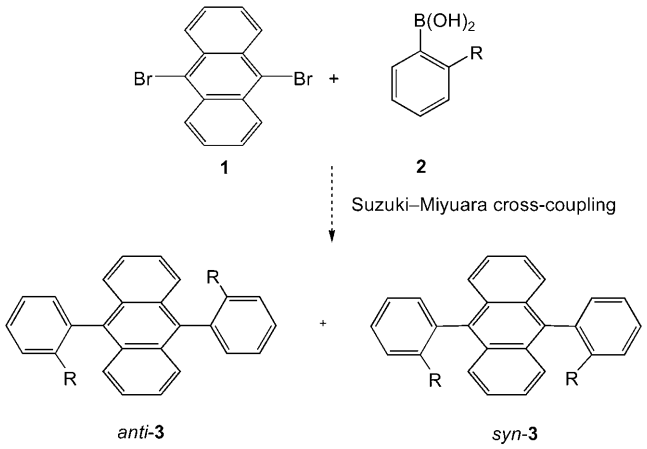
Diphenylanthracene (DPA) was first prepared from anthraquinone by a Grignard reaction, which gives intermediate diols in a yield of 63%, followed by deoxygenation with potassium iodide.[5] In recent years, DPA and its derivatives have been accessed by the Suzuki–Miyaura cross-coupling strategy.[6] The reaction of 9,10-dibromoanthracene (**1**) with arylboronic acids using tetrakis(triphenylphosphine)palladium [$Pd(PPh_4)$] provides diarylanthracenes in yields of up to 95%, but this coupling reaction was only applied to *para*-substituted systems.[7] The corresponding reaction of *ortho*-substituted boronic acids **2** is more challenging due to the large steric interactions of the functional groups R with the anthracene moiety (Scheme 1).

In addition, bis-coupling to give *ortho*-substituted diarylanthracenes **3** is further complicated by the possible formation of isomers. The two substituents of the coupling product **3** can adopt either an *anti* or a *syn* disposition (Scheme 1). Slow rotation around the aryl–aryl axes allows the separation and isolation of the two isomers. The minimum free-energy barrier required for their separation as stable isomers at room temperature is $\Delta G^{\neq} = 96\,kJ\,mol^{-1}$.[8] Dynamic



Scheme 1. Planned formation of diarylanthracenes **3** from 9,10-dibromoanthracene (**1**) and boronic acids **2**.

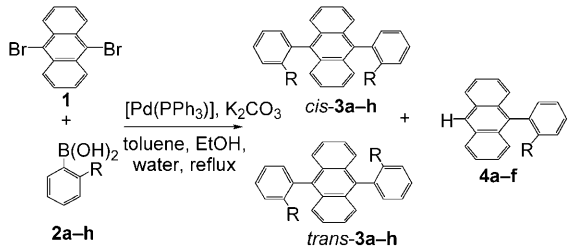
NMR spectroscopy and gas chromatographic (GC) experiments on biaryls were supplemented by computational methods and provided useful information on such rotational processes, which depend on the number and size of the substituents.[9] Tri-*ortho*-substituted biaryl compounds are known to form sufficiently stable rotational isomers because two non-hydrogen substituents are forced to pass each other during rotation.[10] Hence, *ortho*-substituted 9-arylanthracenes should therefore be accessible as isolable stable isomers.

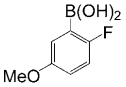
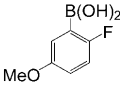
Prompted by our investigations into the synthetic applications of singlet oxygen ($^1O_2$),[11] we became interested in the reversible photo-oxygenation of *ortho*-substituted 9,10-diarylanthracenes to the corresponding 9,10-endoperoxides. Very recently, we succeeded in a *syn–anti* isomerisation by this process, and this was used as the basis for a new and readily available molecular switch triggered by light, air and heating.[12] Herein we report the synthesis of various diarylanthracenes **3**, which can be isolated as conformationally stable *anti* and *syn* isomers, and their unambiguous assignment and characterisation. Furthermore, the substituents exert decisive influences on the physical properties of the isomers and on their reactivity towards singlet oxygen. Finally, the mechanisms of the photo-oxygenation reactions and the *syn–-anti* isomerisations are discussed in detail and provide a clear-cut explanation of the application of 9,10-diarylanthracenes as molecular switches.

Results and Discussion

Synthesis: The diarylanthracenes **3a–h** were synthesised by Suzuki–Miyaura cross-coupling of 9,10-dibromoanthracene (**1**) and the arylboronic acids **2** by using [Pd(PPh$_3$)$_4$] and potassium carbonate under standard conditions (Table 1).[7d] All boronic acids were commercially available except the ethyl and isopropyl derivatives **2b** and **2c**, respectively, which were prepared from the corresponding aryllithium compounds and B(O*i*Pr)$_3$. Interestingly, despite severe steric demand, all the coupling reactions proceeded smoothly and in good yields of up to 80% (Table 1). Modification of the experimental procedure by employing a more intricate catalyst system, which is required for highly substituted biaryls, was therefore unnecessary.[13] Bulkier alkyl substituents at the *ortho* position, for example, the boronic acids **2b** and **2c**, only slightly affected the product yield (Table 1, entries 2 and 3). This is due to the accumulation of mono-coupling products **4**, which occurs when the catalytic process is aborted by dehalogenation.[14]

Table 1. Suzuki–Miyaura cross-coupling reactions of boronic acids **2** with 9,10-dibromoanthracene (**1**) using [Pd(PPh$_3$)$_4$] and K_2CO_3 in toluene, water and ethanol.



Entry	Boronic acid	R	*syn*/*anti* ratio[a]	*syn*-**3** [%][b]	*anti*-**3**[b] [%]	**4**[b] [%]
1	**2a**	Me	42:58	30	48	14
2	**2b**	Et	43:57	34	29	13
3	**2c**	*i*Pr	41:59	34	29	25
4	**2d**	OMe	42:58	36	44	–
5	**2e**	F	41:59	74[c]	[c]	–
6[d]	**2e**	F	40:60	90[c]	[c]	–
7	**2f**[e]	CN	42:58	26	28	32
8	**2g**	CHO	42:58	75[c]	[c]	–
9	**2h**		38:62	33[c]	30	–
10[d]	**2h**		38:62	47[c]	43	–

[a] Determined by ^{1}H NMR spectroscopy of the crude product. [b] Yield of the isolated product after crystallisation or column chromatography. [c] Isomers were not separated. [d] Under microwave irradiation. [e] The boronic acid was converted into the neopentyl ester.[15b]

Attempts to couple the dibromoanthracene with the *o*-cyanophenylboronic acid (**2f**) to afford **3f** failed entirely and resulted in dehalogenation with the formation of anthracene as the sole product. As described by others, Suzuki–Miyaura coupling using *o*-cyanophenylboronic acid (**2f**) suffers from hydrolytic B–C cleavage, which can be circumvented by converting the boronic acid into the corresponding ester.[15] Therefore, coupling by using the neopentyl boronic ester of **2f** in the presence of the same catalyst and base as mentioned before furnished the cyanophenylanthracenes **3f** in acceptable yields (Table 1, entry 7).

We also carried out coupling reactions between **1** and **2** under microwave irradiation. However, with the alkylated boronic acids **2a–d**, only mono-coupling with low yields was observed. On the other hand, with the fluoro derivative **2e**, almost quantitative bis-coupling was achieved, which turned

out to be better than conventional heating (Table 1, entries 5 and 6). To affirm that microwave irradiation promotes the coupling reaction when fluoro substituents are present, we also carried out this reaction with 2-fluoro-5-methoxyphenylboronic acid (**2h**; entries 9 and 10). Again a remarkably higher yield was obtained by microware heating than by the thermal approach.

The bis-coupling products **3** were formed as two conformationally stable isomers, with the *ortho* substituents either adopting a *syn* (with the substituents on the same side of the plane) or an *anti* conformation (with the substituents on opposite sides). The two isomers were easily analysed and distinguished by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy of the crude product mixtures. The NMR spectroscopic analyses of the crude product mixtures revealed that the *anti* isomers are slightly favoured over the *syn* isomers (Table 1, *syn*/*anti* ratio). The second coupling step in the synthesis of the diarylanthracenes **3** may exhibit a weak directing effect because, after bond formation, the structural conformation is frozen.[16] Fortunately, in most cases a precipitate containing only one isomer was formed upon completion of the coupling reaction. The other more soluble isomer was purified by column chromatography. Therefore, the isomers of anthracenes **3a–d** and **3f** were successfully isolated (Table 1) and their conformations assigned. However, it was impossible to separate the isomers of fluoro-substituted **3e** and those of the formyl derivative **3g** and only mixtures of enriched fractions were accessible.

Assignment of the *syn* and *anti* conformations: An unambiguous assignment of the conformation was important for the application of 9,10-diarylanthracenes **3** as molecular switches. Therefore, we conducted detailed structural studies by X-ray analysis (Figure 1 and Table 2) and concomitant evaluation of the ^{1}H NMR spectra (Figure 2).

The *syn* and *anti* conformations of **3a**, **3d** and **3f** can be easily distinguished by the characteristic chemical shifts of the *ortho* substituents in the NMR spectra. In this way, the molecular structure of the isomer of the methyl derivative **3a** that was isolated as a precipitate was identified as the *anti* isomer.

The two methyl substituents are located on opposite faces of the anthracene plane, which is almost orthogonal to the two phenyl groups (Figure 1A). The molecule exhibits a centre of symmetry and the dihedral angles between the 2-methylphenyl ring planes and the anthracene ring system are both 87.25(7)°. In the ^{1}H NMR spectrum of *anti*-**3a** (Figure 2A), the chemical shift of the protons of the CH_3 group (1.93 ppm) is at a higher field than the corresponding protons of the *syn* isomer (1.95 ppm).

X-ray analysis of single crystals of the methoxy derivative **3d** and the cyano compound **3f**, both obtained from the soluble fractions, unequivocally revealed their *syn* conformation (Figure 1B and C). In contrast to *anti*-**3a**, these *syn* isomers exhibit two different dihedral angles between the phenyl rings and the anthracene unit: 89.96(4) and 81.39(4)° for *syn*-**3d** and 86.46(3) and 81.34(3)° for *syn*-**3f**. This

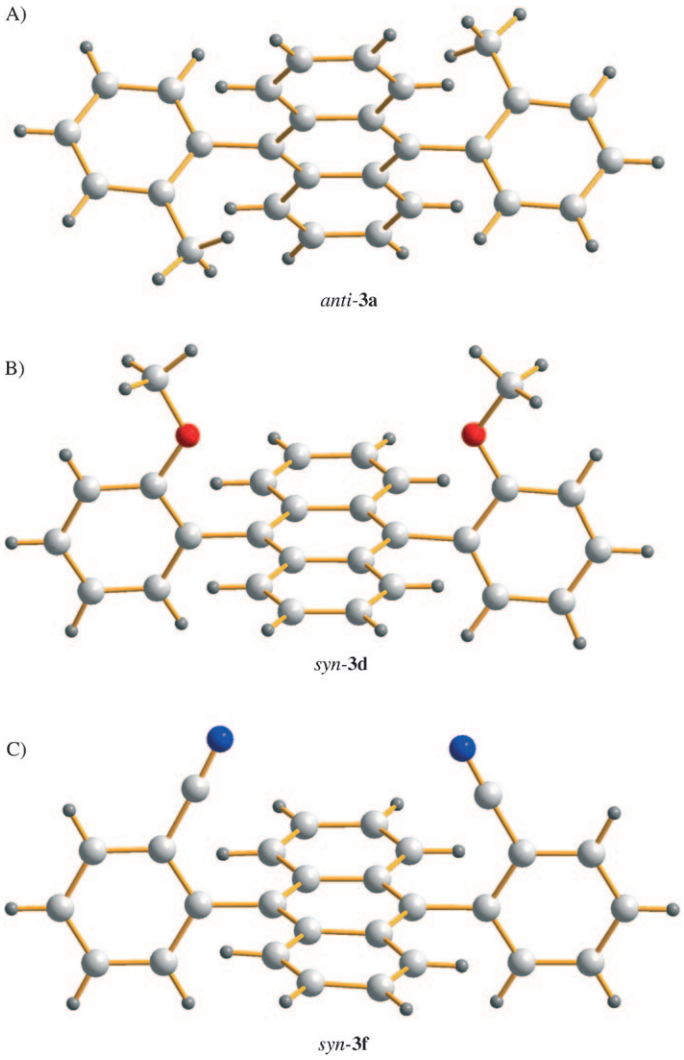


Figure 1. X-ray structures of the anthracenes: A) *anti*-**3a**, B) *syn*-**3d** and C) *syn*-**3f**.

proves the *syn*-configured 9,10-diarylanthracenes **3** have common structures. In analogy to **3a**, the methoxy protons of *anti*-**3d** are shifted slightly to a higher field (Figure 2B), whereas the characteristic proton (6-H_{phenyl}) of the cyanophenylanthracene *anti*-**3f** appears at a lower field (Figure 2C). Because the protons of the methyl groups of **3a** and **3d** lie above the anthracene plane, the presumption of a shielding effect due to the ring current is reasonable. The resulting shift to a higher field is clearly more strongly pronounced for the *anti* isomers. The pertinent phenyl proton of the cyano derivative **3f**, on the other hand, is farther away from the centre of the shielding part of the plane, which inverts the effects on the chemical shifts of the *syn* and *anti* isomers.

Next we thoroughly investigated the physical properties of the *syn*- and *anti*-configured anthracenes **3a–h**. Interestingly, the *anti* isomers showed distinctly different behaviour compared with their corresponding *syn* isomers (Table 3).

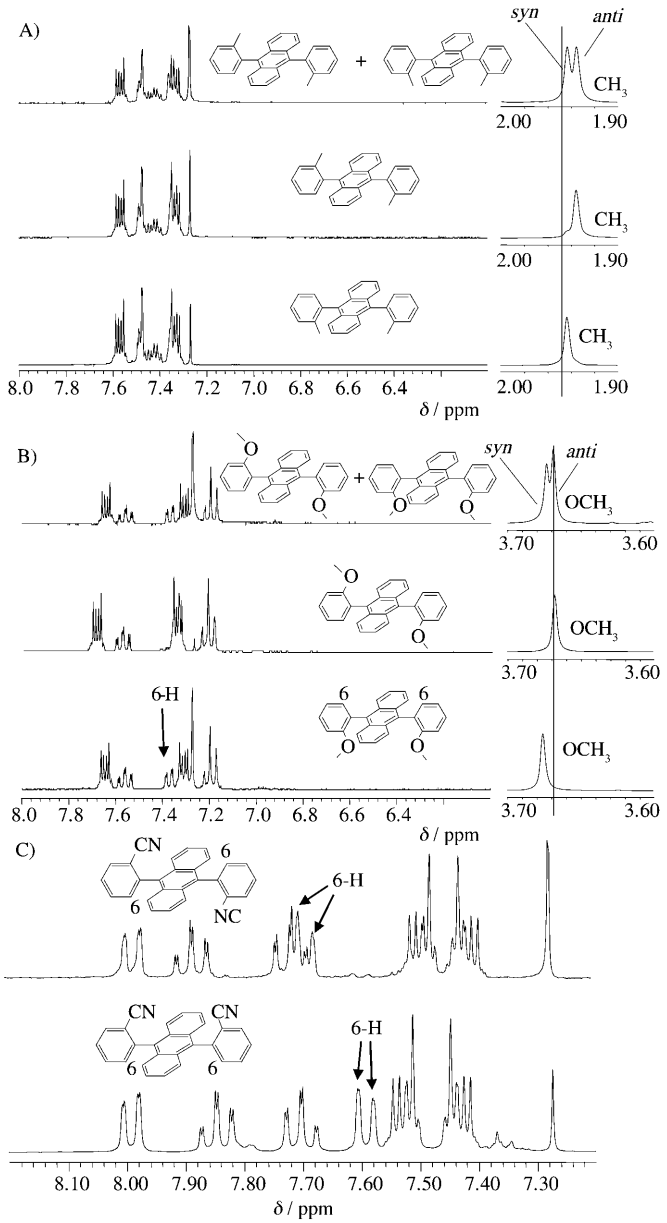


Figure 2. ^{1}H NMR spectra of isolated *syn* and *anti* isomers of the anthracenes: A) **3a**, B) **3d** and C) **3f**.

1) They exhibit lower solubility in common organic solvents.
2) Their melting points are higher.
3) Their reactivity towards singlet oxygen is strongly diminished.[12]

We therefore concluded that these properties are unique for 9,10-diarylanthracenes **3**, which allows us to predict that the *anti* isomer is generally obtained from a precipitate, whereas the *syn* isomer can be isolated from the remaining solution. These findings are not only important for the synthesis of substituted anthracenes, but also for their application as molecular switches.

Table 2. X-ray crystallographic and refinement data for *anti*-**3a**, *syn*-**3d**, *syn*-**3f** and the endoperoxide **5a**.

	anti-**3a**	*syn*-**3d**	*syn*-**3f**	**5a**
formula	$C_{28}H_{22}$	$C_{28}H_{22}O_2$	$C_{28}H_{16}N_2$	$C_{28}H_{22}O_2$
M_r [g mol^{-1}]	358.46	390.46	380.43	390.46
crystal size [mm]	0.5×0.25×0.1	0.5×0.38×0.3	0.5×0.34×0.3	0.3×0.16×0.1
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$	$Pbca$	$P2_1/c$	$C2/c$
a [Å]	11.733(4)	17.4125(9)	10.9801(10)	16.9064(14)
b [Å]	7.6696(15)	11.1909(5)	14.1658(15)	16.3861(19)
c [Å]	12.403(4)	21.1510(12)	12.9428(13)	14.9094(12)
α [Å]	90	90	90	90
β [Å]	117.27(2)	90	92.150(8)	96.438(7)
γ [Å]	90	90	90	90
V [Å^3]	992.1(5)	4121.5(4)	2011.7(3)	4104.3(7)
ρ_{calcd} [g cm^{-3}]	1.200	1.259	1.256	1.264
Z	2	8	4	8
μ [mm^{-1}]	0.068	0.078	0.074	0.078
F (000)	380	1648	792	1648
θ range	1.98–24.76	1.93–25.00	1.86–25.00	1.74–24.75
index ranges	$-13\le h\le 13$ $-8\le k\le 8$ $-14\le l\le 14$	$-20\le h\le 20$ $-13\le k\le 12$ $-25\le l\le 25$	$-13\le h\le 12$ $-16\le k\le 16$ $-15\le l\le 15$	$-19\le h\le 19$ $-19\le k\le 19$ $-17\le l\le 17$
reflns coll.	5717	25136	12604	24802
indep. reflns	1669	3630	3504	3483
R_{int}	0.0748	0.0340	0.0489	0.1054
parameters	161	338	320	338
S on F^2	0.819	1.054	0.936	0.0864
R_1 $[F>2\sigma(F)]$[a]	0.0431	0.0388	0.0357	0.0420
wR_2 (all data)[b]	0.0812	0.1060	0.0899	0.0876

[a] $R_1=\Sigma\,|F_o|-|F_c|/\Sigma\,|F_o|$. [b] $wR_2=[\Sigma(F_o^2-F_c^2)/\Sigma w(F_o)^2]^{1/2}$.

Table 3. Comparison of the physical properties of the *syn* and *anti* isomers of **3**.

Anthracene	Solubility[a] [M]		Melting point [°C]	
	syn	*anti*	*syn*	*anti*
3a	5.7×10^{-2}	9.3×10^{-3}	300	330
3b	3.9×10^{-2}	6.7×10^{-3}	222	297
3c	8.4×10^{-2}	1.3×10^{-2}	263	327
3d	3.6×10^{-2}	3.5×10^{-3}	308	318
3e	0.136[b]	0.136[b]	265[b]	265[b]
3f	8.5×10^{-3}	6.9×10^{-3}	315	>350
3g	3.8×10^{-2}[b]	3.8×10^{-2}[b]	[c]	[c]
3h	3.9×10^{-2}[b]	1.3×10^{-2}	275[b]	275

[a] In $CHCl_3$. [b] Isomers not separated. [c] Decomposition (200 °C).

In summary, we have synthesised 9,10-diarylanthracenes **3a–g** by Suzuki–Miyaura coupling of 9,10-dibromoanthracene (**1**) with the corresponding boronic acids **2** in good yields. The *syn* and *anti* isomers were separated in most cases by simple crystallisation and their conformations were assigned unambiguously by characteristic signals in the ^{1}H NMR spectra and X-ray analysis. Furthermore, the remarkable differences in their melting points and solubility should correlate with distinctive 3D crystal-packing structures, which will be discussed in the next section.

Crystal-packing structures: It is well known that substituted polyacenes can adopt two common packing structures, namely a herringbone and a π-stacking arrangement.[17] Indeed, anthracene *anti*-**3a** arranges in a herringbone packing with a translated interplanar distance of 7.669 Å and an interplanar angle of 85.33° between the two nearest neighbouring anthracene rings (Figure 3A).[18]

Analogously, *anti*-**3d** resembles a herringbone structure with a larger interplanar distance of 8.330 Å (Figure 3C).[19] In contrast, *syn*-**3d** forms a non-typical packing motif. The shortest cell axis is 11.19 Å, which exceeds the prerequisites for typical herringbone packing.[17a,b] The packing in Figure 3B also indicates that anthracene molecules adopt more than two different planes within one unit cell. The herringbone-type crystal packing of *syn*-**3f**, which is shown in Figure 3D, reveals that the shortest interplanar distance of 10.98 Å is remarkably long. However, a shorter distance of only 3.264 Å is found between two neighbouring anthracenes located along the same axis in the same unit cell (Figure 3C). In contrast to *anti*-**3a**, these neighbouring molecules align in a head-to-head and tail-to-tail fashion because the cyano substituents are oriented in opposite directions (Figure 3C). Although we could not clearly deduce π–π stacking effects from these dyads because the planes are not sufficiently stacked above each other, the short distance might account for a certain degree of π overlap. The different packing behaviour of these three crystals unequivocally shows that the conformation determines the intermolecular packing arrangement, which is an important prerequisite for the control of π orbital overlap in organic semiconductors.[20] Therefore, the 9,10-diarylanthracenes **3** are not only interesting molecular switches, but might find future applications in molecular electronics.

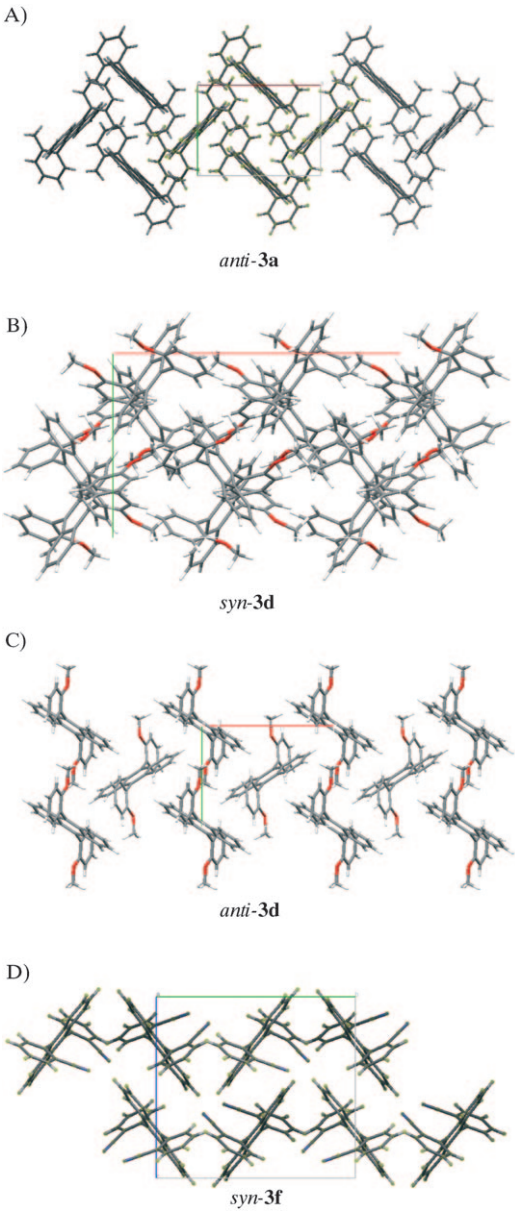


Figure 3. 3D crystal-packing structures of the diarylanthracenes: A) *anti*-**3a** (view along the *c* axis), B) *syn*-**3d** (view along the *c* axis), C) *anti*-**3d** (view along the *c* axis) and D) *syn*-**3d** (view along the *a* axis).

Thermal isomerisation: The *ortho* substituents of the diarylanthracenes act as brakes for the rotation around the aryl bonds and thus the rotamers are stable at room temperature.[12] The experimental value for the rotational barrier increases from 75 kJ mol^{-1} for *o*-H to 120 kJ mol^{-1} for *o*-CH_3.[21]

In accordance with these values, it should be possible to monitor the thermal interconversion of *ortho*-fluoro-substituted anthracenes by ^{19}F NMR spectroscopy at elevated temperatures. It was impossible to isolate anthracene *anti*-**3e** as a single isomer. However, we were able to precipitate the structurally similar *ortho*-fluoro-substituted anthracene **3h** directly after the coupling step. Hence, we studied the thermal interconversion starting from the *anti* isomer of **3h** (Figure 4). The half-life for *anti*-**3h** to reach the thermal equilibrium at 343 K in $C_2D_2Cl_4$ is 4 h. The isomer ratios at thermal equilibrium for the two fluoro derivatives **3e** and **3h** turned out to be slightly solvent dependent, as shown in Table 4. It can be seen that the *anti* species are favoured in less polar solvents because its calculated dipole moment is significantly smaller than the dipole moment of the corresponding *syn* isomer (Table 4). This behaviour provides an additional characteristic for distinguishing between the two possible conformations.

In contrast, the presence of alkyl and alkoxy substituents in the *ortho* positions leads to an increase in the temperature of thermal isomerisation and investigation by NMR spectroscopy in solution becomes impossible. The pure, neat, solid *syn* isomers of the *o*-methyl (**3a**) and *o*-methoxy (**3d**) diarylanthracenes isomerised rapidly to a *syn*/*anti* mixture at $T \approx 590$ K, which is above their melting points. NMR spectroscopic analysis after cooling indicated a strong prevalence for the *anti* form (>95%). Determination of the isomer ratio at the temperature of interconversion (590 K), however, was not possible. We expect that the more bulky alkyl substituents, compared with the smaller fluoro atom,

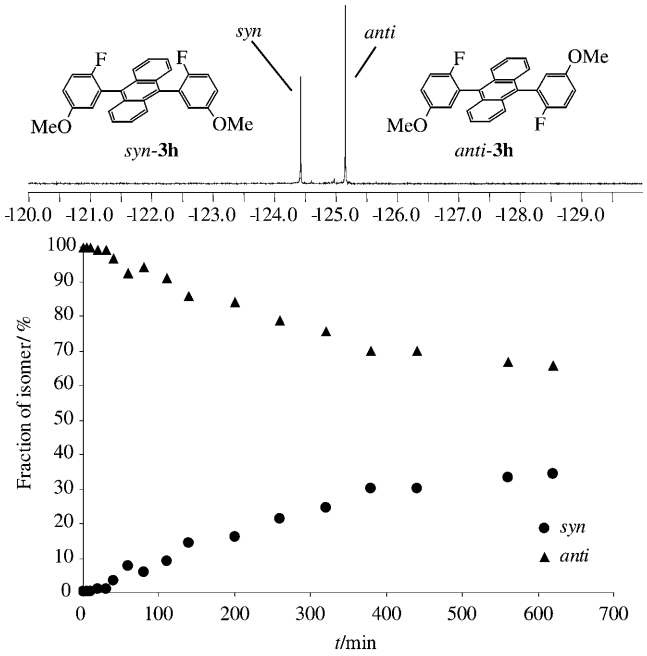


Figure 4. Change in the molar fractions of the *anti* and *syn* isomers of **3h** at 343 K studied by ^{19}F NMR spectroscopy in $C_2D_2Cl_4$ starting from the pure *anti* form (bottom). ^{19}F NMR spectrum of a mixture of *syn* and *anti* isomers (top).

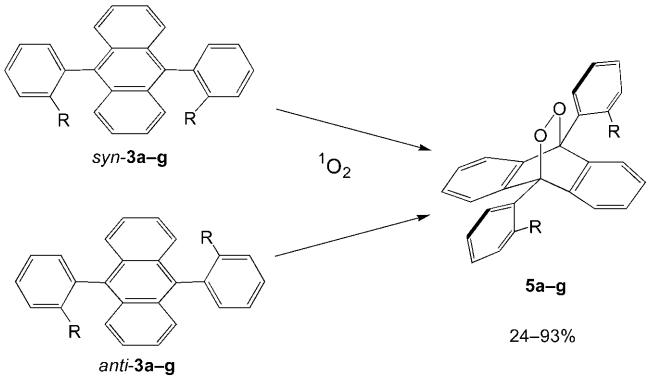
Table 4. Dependence of the *syn*/*anti* ratio on the solvent after equilibration.

Anthracene	*syn*/*anti* ratio			Calcd dipole moment
	toluene[a]	$C_2H_2Cl_4$[b]	DMSO[c]	[D][d]
3e	41:59	41:59	55:45	2.62 (*syn*) 0.03 (*anti*)
3h	38:62	38:62	47:53	3.49 (*syn*) 0.59 (*anti*)

[a] For toluene: $\pi^*=0.54$, $\varepsilon=2.4$ (π^* is the polarisability and ε is the dielectric constant of the solvent). [b] For $C_2H_2Cl_4$: $\pi^*=0.9$, $\varepsilon=8.2$. [c] For DMSO: $\pi^*=1.0$, $\varepsilon=49$. [d] Computed by the PM3 method.

account for the stronger preference of the *anti* isomer. Note that *syn* and *anti* isomers have different phase-transition temperatures (Table 3), which might affect the isomeric ratios as well. For example, *syn*-**3a** melts upon heating to 573 K and then rotates to the *anti* form, which has a melting point above the heating temperature. The different phase transition regions could account for the almost exclusive accumulation of the *anti* species, which is very important for the application of anthracenes **3** as molecular switches.

[4+2] Cycloaddition of singlet oxygen: Photo-oxygenation reactions of the diarylanthracenes **3a–h** were carried out in oxygen-saturated $CDCl_3$ solutions in the presence of Methylene Blue (MB) as photosensitiser by irradiation with a sodium lamp. The reactions of the *syn* and *anti* isomers were conducted separately (Scheme 2). The less soluble *anti* isomers required highly diluted solutions, whereas the photo-oxygenation reactions of the more soluble *syn* isomers could be carried out on larger scales.



Scheme 2. Reactions of the *syn* and *anti* isomers of **3** with singlet oxygen.

All the photo-oxygenation reactions afforded products that could be isolated and conformationally assigned, except for the isomeric mixture of the formyl derivative **3g**, which decomposed under the reaction conditions. Several interesting findings emerged from a comparison of the photo-oxygenation reactions of *syn* and *anti* isomers.

At first, both precursors provide the same 9,10-endoperoxide as the main product with the substituents located in the *anti* orientation with respect to the oxygen atoms. The molecular structure was again confirmed by X-ray analysis of the methyl derivative **5a** (Figure 5, Table 2), obtained by the photo-oxygenation of both the *syn* and *anti* isomers of **3a**. It can be seen that the peroxo bridge creates a boat con-

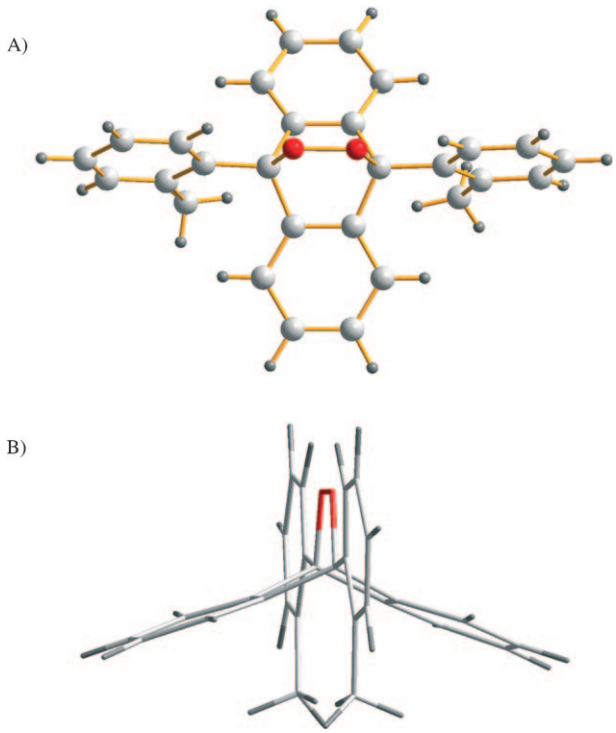


Figure 5. X-ray structure of the endoperoxide **5a**: A) top view and B) side view.

formation and that the two phenyl rings are in the same plane as the bridging oxygen atoms.

NMR spectroscopic analysis of the crude reaction mixtures was carried out to disprove the formation of the isomeric 9,10-endoperoxide in which the two *ortho* substituents are oriented *anti* to each other. The spectra of such species should be identifiable by the existence of two different sets of chemical shifts for the *ortho* substituents. However, only one set of symmetrical signals was obtained, which proves the exclusive formation of *syn*-endoperoxides. This is understandable on consideration of the steric repulsion between the oxygen atom and a proximal *ortho* substituent. The exclusive formation of *syn*-endoperoxides **5a–h**, however, implies the isomerisation of the *anti*-configured starting materials **3** during or after (see below) the photo-oxygenation reaction, although rotation around the C–C bond is strongly hindered, as described in the previous section. Therefore, the *anti* isomers act as $^1O_2$-triggered molecular switches. To study the possible thermal isomerisation of the endoperoxides, solutions of the methyl and fluoro endoperoxides (**5a** and **5e**, respectively) were heated at temperatures that range from 60–100 °C in $C_2D_2Cl_4$ and the conversion was monitored by NMR spectroscopy. Both endoperoxides, however, reconverted exclusively to the parent anthracenes and signals corresponding to the *anti*-endoperoxide were not detected. Interestingly, signals of the *anti* isomer of the fluoro-substituted anthracene **3e** appeared and increased in intensity during the heating experiment, which shows that rotation of the parent *syn*-anthracene proceeds sufficiently quickly on the NMR spectroscopy timescale, but not the rotation of the endoperoxide. The rotational barrier around the C–C axes of the endoperoxides should exceed the activation energy for thermolysis (100–130 kJ mol^{-1}) and the rotation cannot compete with the cleavage.[22] We therefore conclude that the rotation, as above mentioned, should occur during and not after the photo-oxygenation reaction.

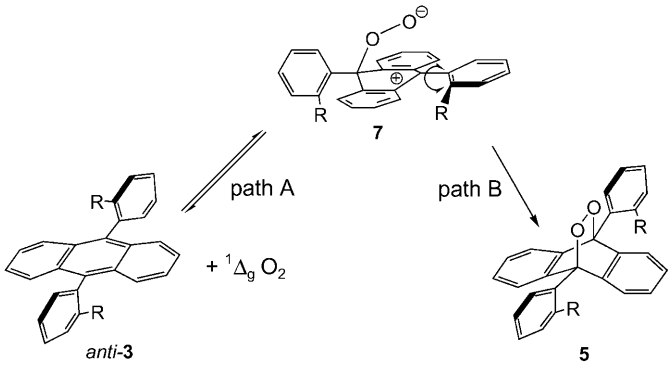
The second finding emerged from the observation that *syn* and *anti* isomers are converted with different yields and require different reaction times. Reaction times were determined by UV spectroscopy and thin-layer chromatography and denote the time required for complete conversion of the starting material. The value does not linearly correlate with the rate of formation because some decomposition products were formed.[23] As shown in Table 5, *syn* isomers react with higher yields and higher conversion rates than their *anti* counterparts. The extent of this disparity depends on the size of the substituents as a bulkier substituent on both sides of the anthracene plane shields the attack of $^1O_2$ more strongly. In addition, in general, increasing bulkiness causes a decrease in yield (compare entries 1, 3 and 5 in Table 5). A combination of both steric and electronic influences of the substituents might explain the exceptional case of the photo-oxidation of the cyano-substituted anthracene **3f**. The *syn* isomer of **3f** requires a longer conversion time than the other *syn* isomers and the yield is correspondingly smaller. The reduced reactivity of the corresponding *anti* isomer is countered by the relatively small and stiff substituent. Thus, the difference between the yields of the *syn* and *anti* isomers is smaller for **3f** than for **3b** and **3c**, the latter two having the more flexible and bulky substituents. The decrease in reactivity, in general, is associated with a drop in yield due to the competitive formation of other side-products (see below).[23]

Table 5. Reactions of anthracenes **3** with singlet oxygen to give the endoperoxides **5** and **6**.

Entry	Anthracene[a]	t[b] [h]	**5**[c] [%]	**6**[c] [%]
1	*syn*-**3a**	12	85	–
2	*anti*-**3a**	48	49	10
3	*syn*-**3b**	14	53	–
4	*anti*-**3b**	60	27	27
5	*syn*-**3c**	12	24	–
6	*anti*-**3c**	96	10	16
7	*syn*-**3d**	12	80	–
8	*anti*-**3d**	48	61	–
9	**3e**	12	93	–
10	*syn*-**3f**	48	56	–
11	*anti*-**3f**	80	37	–
12	**3g**[d]	34	–	–
13	*anti*-**3h**	24	75	–

[a] Saturated solutions of **3** (10^{-2}–10^{-3} M) in $CDCl_3$ in the presence of methylene blue. [b] Time for complete comversion. [c] Yield of the isolated product after column chromatography. [d] Decomposition.

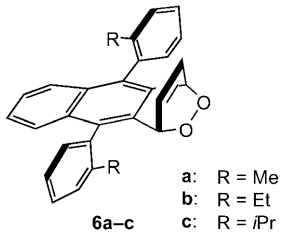
The high rotational barriers around the C–C bond mentioned in the above section are surmounted by the formation of an intermediate **7** during the oxidation with $^1O_2$ (Scheme 3). A control reaction with anthracene **3e** in which singlet oxygen was chemically generated from H_2O_2 and MoO_4^{2-} in the dark[24] afforded the same yield of 9,10-endoperoxide **5e** as with the light-induced procedure. A second control reaction, conducted with anthracene *anti*-**3a** in the absence of oxygen under irradiation with visible light, caused no conversion or isomerisation at all. Thus, the *syn*/*anti* isomerisation is only possible in the presence of $^1O_2$. These observations confirm a reaction pathway that is initiated by excited oxygen with anthracene in the ground state and passes through transition states towards and beyond zwitterion **7**. Supported by our previous results, intermediate



Scheme 3. Proposed structure of the zwitterionic intermediate **7**, which can reconvert to the anthracene **3** or react to give the 9,10-endoperoxide **5**.

7 exhibits bipolar and not biradical character with an almost coplanar alignment of the benzene ring relative to the anthracene plane.[22] In the progression, this intermediate might either reconvert to oxygen and the anthracene in the *anti* conformation (path A) or the benzene ring may flip through the dihedral plane to afford the endoperoxide **5** with the substituents in a *syn* conformation (path B). The energy of at least one of the two transition states lying on either side of the intermediate is essentially higher than the rotation barrier for the interconversion from the *anti* to the *syn* form. This is supported by theoretical studies on the addition of $^1O_2$ to anthracene in which the energy of the transition state was calculated to be 123 kJ mol^{-1}.[25] The experimental value of the rotation barrier of anthracene **3a** in the ground state, on the other hand, is 120 kJ mol^{-1}.[21b] Electron-withdrawing groups such as CN (**3f**) or CHO (**3g**) destabilise the intermediate **7** and the equilibrium is shifted away from the endoperoxide **5** towards the parent anthracene **3**. Increasing bulkiness of the substituents clearly affects the reactions of both the *syn* and the *anti* isomers. This is in accordance with our proposed mechanism because a half-rotation towards coplanarity ($\approx$90°) is required for both isomers.

Another unexpected result was observed during the photo-oxygenation of anthracenes with larger substituents in the *anti* conformation (e.g., *anti*-**3b**). In addition to the 9,10-endoperoxide **5** and unidentified decomposition products, another species was competitively formed with increasing size of the substituent. ^{1}H NMR spectroscopy and HRMS spectrometry confirmed that these products are the 1,4-endoperoxides **6** (Scheme 4). The substituents still adopt an



Scheme 4. Structures of the 1,4-endoperoxides **6**.

anti conformation, so no rotation around the aryl–aryl bond has occurred. In accordance with our proposed mechanism, the rotational process requires attack at the centre ring, which forces the adjacent phenyl ring at the 9-position to rotate. On the other hand, a different (concerted) mechanism has previously been postulated for the 1,4-addition to acenes, which may also apply to the 1,4-addition to *anti* anthracenes **3**.[26] This mechanism would not require a rotation. 1,4-Endoperoxides **6** were not obtained from *anti*-**3d–f**, probably due to a stronger propensity to isomerise under the reaction conditions.

Compounds **6** belong to the rare class of endoperoxides in which the most electron-rich carbon atoms, C-9 and C-10, are still sp^2-hybridised and the oxygen has attacked the outer ring. In contrast to the previously known examples of such 1,4-anthraceneendoperoxides, to the best of our knowledge, compounds **6** provide the first examples in which the two sp^3 carbon atoms are unsubstituted.[27] This new class of endoperoxides exhibits a remarkable stability and the parent anthracenes *anti*-**3a–c** were recovered only after heating above 100 °C.

Thermolysis of the endoperoxides: The endoperoxides **5a–d** and **5f** were heated at reflux in toluene to regenerate the parent anthracenes. We have previously investigated the kinetics of the cycloreversion of such compounds.[22] The half-lives under the above conditions range from 10 to 20 min. Without exception, the anthracenes **3a–d** and **3f** were obtained in quantitative yields without the formation of by-products. Interestingly, thermolysis exclusively furnished the parent anthracenes with a *syn* conformation. In contrast to the forward reaction, in which anthracenes with the *anti* conformation switched to *syn* upon the addition of $^1O_2$, the endoperoxides **5a–d** and **5f** did not isomerise. This finding further supports the assumption that microreversibility for the reaction of singlet oxygen with anthracenes **3** is not fulfilled. The sequence of photo-oxygenation and thermolysis therefore constitutes the first stage of a molecular switch from *anti*-**3** to *syn*-**3**. In addition, it represents a simple synthetic strategy for the preparation of *syn* products selectively from an unselective C–C coupling reaction. Heating at increased temperatures (>300 °C) finally allowed isomerism back to the *anti* rotamers.[12]

Finally, we investigated the thermolysis of the fluoro-substituted endoperoxides **5e** and **5h**. Interestingly, these two endoperoxides reacted less selectively to give *syn*/*anti* mixtures of anthracenes **3e** and **3h**, respectively, in high yields. This can be rationalised by the smaller fluoro substituents, which, in contrast to alkyl-substituted anthracenes **3a–c**, allow rotation around the aryl–aryl bond at the temperature of thermolysis (110 °C). To overcome this problem, photolysis with UV light offers a valuable alternative to thermal cleavage.[28] We investigated the irradiation of endoperoxide **5e** at 254 nm at room temperature. Although the yield of anthracene **3e** was lower due to radical pathways during the photolysis,[28a] the selectivity in favour of the *syn* isomer was very high. Thus, rotation around the aryl–aryl bond is not induced in the photoexcited state of endoperoxides. In consequence, the cleavage of oxygen proceeds with conservation of the *syn* conformation and further rotation occurs only under thermal conditions at higher temperatures. This result is not only important for the mechanistic understanding of the cleavage of endoperoxides, it should also provide the basis for new molecular switches operating under irradiation at lower temperatures.

Conclusion

Ortho-substituted 9,10-diarylanthracenes, which are accessible as conformationally stable isomers, are an interesting

new class of photochromic compounds. They are easily obtained from Suzuki–Miyaura cross-coupling reactions in one step in good yields and can be isolated by crystallisation. *Syn* and *anti* isomers were distinguished unequivocally by NMR spectroscopy and X-ray structures prove their relative conformations. In addition, the two conformers differ strongly in their physical and chemical properties and interconvert at high temperatures. Kinetic data for this isomerisation process were obtained by time-dependent NMR spectroscopy studies for the first time.

Both classes of *o*-9,10-diarylanthracene isomers react with singlet oxygen to form the same endoperoxide as the main product. This oxidation is accompanied by rotation around the aryl–aryl bond and strongly depends on the electronic and steric natures of the substituents. A new class of 1,4-endoperoxides was isolated as byproducts. Clear evidence for the stepwise addition of $^1O_2$ via zwitterionic intermediates to the anthracene provided valuable information on the mechanism of such oxidation reactions. In summary, 9,10-diarylanthracenes are ideal substrates for use as molecular switches that operate under mild and environmentally friendly conditions.

Experimental Section

General methods: All reagents were purchased from Aldrich and used without further purifications. Solvents were dried according to standard procedures. Column chromatography was performed by using Merck silica gel 60. TLC was performed on silica gel coated aluminium foils (0.25 mm thick, 60 F_{254}, Merck, Germany). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer at 300 and 75 MHz, respectively. Deuteriochloroform was used as the internal standard ($\delta = 7.26$ and 77.0 ppm, respectively). ^{19}F NMR spectra were recorded on a Bruker AC 300 spectrometer at 282.4 MHz using trichlorofluoromethane as the internal standard. Melting points were determined on a Barnstaed/Electrothermal 9100 apparatus. The solubility was determined by measurement of the extinction coefficients of saturated solutions by using a Unicam UV3 spectrometer. The X-ray analyses were performed on an Imaging Plate Diffraction System IPDS-2 (Stoe) at 210 K with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The intensity data were corrected for absorption and extinction. The structures were solved with SHELXS-97[29] using direct methods and refined against F^2 by full-matrix least-squares procedures with SHELXL-97.[30] The non-hydrogen atoms were refined anisotropically. All hydrogen atoms could be located from the difference Fourier maps. They were refined isotropically by using a riding model.

CCDC-692386 (*anti*-**3a**), CCDC-692384 (*syn*-**3d**), CCDC-692383 (*syn*-**3f**) and CCDC-692385 (**5a**) 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.

2-Ethylphenylboronic acid (2b): A solution of 2-bromo-1-ethylbenzene (2.17 g, 11.7 mmol) in dry THF was cooled to −78 °C under argon. Then *t*BuLi (15% in pentane, 23.5 mmol) was added dropwise and the solution was cooled for another 2 h. The solution was transferred through a cannula to a solution of triisopropyl borate (6.62 g, 35.2 mmol) in dry THF, which was also cooled to −78 °C. The reaction mixture was kept at RT overnight and quenched with HCl (2 M, 20 mL). After stirring for 30 min, the organic phase was separated and the aqueous phase was washed three times with diethyl ether. The combined organic fractions were dried with Na_2SO_4 and the solvent was removed under vacuum. The residue was suspended in ethanol (30 mL), NaOH (1.6 g) was added and the mixture was stirred for 30 min. After evaporation of the solvent, water (30 mL) and diethyl ether (30 mL) were added. The aqueous phase was separated and acidified with 2 M HCl and extracted several times with diethyl ether to collect the product after drying and evaporation to give a white solid (1.35 g, 77% yield). M.p. 113 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.39$ (t, $J = 7.5$ Hz, 3H; 8-H), 3.26 (q, $J = 7.5$ Hz, 2H; 7-H), 7.33–7.38 (m, 2H; 3-H, 5-H), 7.52 (dt, $J = 7.5$, 1.5 Hz, 1H; 4-H), 8.25 ppm (dd, $J = 7.5$, 1.7 Hz, 1H; 6-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 17.5$ (q, C-8), 28.8 (t, C-7), 125.2 (d, C-6), 129.2 (d, C-4), 132.3 (d, C-3), 137.4 (d, C-5), 152.9 ppm (s, C-2); IR (KBr): $\tilde{\nu} = 3214$, 2965, 1597, 1445, 1345, 1293, 758, 715, 692 cm^{-1}; MS (EI): *m*/*z*: 150 $[M]^+$, 106 $[M-B(OH)_2]^+$.

2-Isopropylphenylboronic acid (2c): By using the same procedure as for **2b**, 2-bromo-1-isopropylbenzene (2.36 g, 11.75 mmol) afforded the boronic acid **2c** as a white solid (1.49 g, 77%). M.p. 88–89 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.18$ (d, $J = 6.8$ Hz, 6H; 8-H), 3.2 (q, $J = 6.8$ Hz, 1H; 7-H), 7.32 (dt, $J = 7.4$, 1.3 Hz, 1H; 5-H), 7.47 (d, $J = 6.9$ Hz, 1H; 3-H), 7.57 (dt, $J = 7.3$, 1.4 Hz, 1H; 4-H), 8.19 ppm (dd, $J = 7.5$, 1.2 Hz, 1H; 6-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 24.8$ (q, C-8), 31.1 (d, C-7), 125.2 (d, C-4, C-6), 132.3 (d, C-3), 137.1 (d, C-5), 157.2 ppm (s, C-2); IR (KBr): $\tilde{\nu} = 3216$, 2963, 1597, 1443, 1338, 1293, 765, 695 cm^{-1}; MS (EI): *m*/*z*: 164 $[M]^+$, 149 $[M-CH_3]^+$, 131 $[M-CH_3-H_2O]^+$.

General procedure for the synthesis of diarylanthracenes 3a–h: In a 100 mL three-necked round bottom flask, the boronic acid **2** (2.5 equiv, 7.35 mmol), 9,10-dibromoanthracene (**1**) (990 mg, 1 equiv, 2.94 mmol) and K_2CO_3 (3.28 g, 23 mmol) were dissolved in toluene (40 mL), ethanol (8 mL) and water (16 mL). Argon was bubbled vigorously through the solution for 5 min followed by the addition of tetrakis(triphenylphosphine)palladium (254 mg, 0.2 mmol), after which argon was bubbled again through the solution for another 5 min. The solution was then heated at reflux for 24 h. For all the anthracenes, except **3e** and **3g**, a solid was formed after cooling and was separated by filtration and recrystallised from chloroform. The structure of the solid was assigned to the *anti* isomer for all the anthracenes on the basis of distinct NMR data and X-ray crystal structures. The filtrate (a mixture of both isomers and monocoupling products) was washed with brine, dried with Na_2SO_4 and the solvent was removed under reduced pressure. The residue was subjected to column chromatography to afford the *syn* isomer. In the case of compounds **3e** and **3g**, the crude reaction solutions were treated analogously.

Microwave-assisted synthesis of diarylanthracenes: In a 80 mL quartz flask, the boronic acid **2** (1.2 equiv, 3.6 mmol), 9,10-dibromoanthracene (**1**) (495 mg, 1 equiv, 1.47 mmol) and K_2CO_3 (1.64 g, 11 mmol) were dissolved in dimethoxyethane (DME) (25 mL), ethanol (5 mL) and water (11 mL). Argon was bubbled vigorously through the solution for 5 min followed by the addition of tetrakis(triphenylphosphine)palladium (125 mg, 0.1 mmol), after which argon was bubbled again through the solution for another 5 min. The flask was placed in a microwave reactor (CEM, Labmate) and the reaction mixture was irradiated at 100 W for 30 min without external cooling. The irradiation power was coupled with the temperature to keep a constant reaction temperature of 100 °C. The maximum pressure was set to 12 bar. Work up was carried out in the same way as for the thermal procedure.

***syn*-9,10-Bis(2-methylphenyl)anthracene (*syn*-3a)**: Yield: 321 mg (30%); $R_f = 0.21$ (hexane/ethyl acetate 50:1); m.p. 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.95$ (s, 6H; Me), 7.4–7.5 (m, 6H; 2-H, 3-H, 6-H, 7-H, 3-H Ar), 7.32–7.3 (m, 6H; 4-H Ar, 5-H Ar, 6-H Ar), 7.56–7.61 ppm (m, 4H; 1-H, 4-H, 5-H, 8-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.7$ (q, Me), 125.1 (d, C-2, C-3, C-6, C-7), 125.8 (s, C-4 Ar), 126.7 (d, C-1, C-4, C-5, C-8), 127.8 (s, C-11, C-12, C-13, C-14), 129.7, 130.0, 131.3 (3 d, C-3 Ar, C-5 Ar, C-6 Ar), 136.2, 137.8, 138.4 ppm (3 s, C-9, C-10, C-1 Ar, C-2 Ar); IR (KBr): $\tilde{\nu} = 3056$, 3012, 2918, 1489, 1438, 1382, 941, 771, 753 cm^{-1}; MS (MALDI-TOF): *m*/*z* (%): 358 (5) $[M]^+$.

***anti*-9,10-Bis(2-methylphenyl)anthracene (*anti*-3a)**: Yield: 504 mg (48%); m.p. 330 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.93$ (s, 6H; Me), 7.30–7.35 (m, 6H; 2-H, 3-H, 6-H, 7-H, 3-H Ar), 7.38–7.48 (m, 6H; 4-H Ar, 5-H Ar, 6-H Ar), 7.52–7.59 ppm (m, 4H; 1-H, 4-H, 5-H, 8-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.8$ (q, Me), 125.1 (d, C-2, C-3, C-6, C-7), 125.8 (s, C-4 Ar), 126.7 (d, C-1, C-4, C-5, C-8), 127.8 (s, C-11, C-12, C-13, C-14), 129.7, 130.0, 131.4 (3 d, C-3 Ar, C-5 Ar, C-6 Ar), 136.3, 137.9,

138.4 ppm (3 s, C-9, C-10, C-1 Ar, C-2 Ar); IR (KBr): $\tilde{\nu}$ = 3058, 3012, 2919, 1491, 1438, 1381, 942, 768, 750 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{22}$ (358.3): C 93.81, H 6.19; found: C 93.61, H 6.27.

9-(2-Methylphenyl)anthracene (4a): Yield: 107 mg (14%); R_f = 0.20 (hexane/ethyl acetate 50:1); m.p. 210°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.90 (s, 3H; Me), 7.27–7.29 (m, 1H), 7.33–7.43 (m, 3H), 7.45–7.48 (m, 4H), 7.50–7.56 (m, 2H), 8.07 (d, J = 8.4 Hz, 2H; 4-H, 5-H), 8.52 ppm (s, 1H; 10-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.7 (q, Me), 125.1, 125.8, 126.3, 126.5, 127.8, 128.4 (6 d, C-1, C-2, C-3, C-4, C-5, C-6, C-7, C-8, C-10, C-3 Ar, C-5 Ar), 129.9 (s, C-11, C-14), 130.0, 131.2 (2 d, C-6 Ar, C-4 Ar), 131.4 (s, C-12, C-13), 136.4, 137.8, 138.1 ppm (3 s, C-9, C-1 Ar, C-2 Ar); IR (KBr): $\tilde{\nu}$ = 3052, 2920, 2855, 1489, 1440, 1380, 1354, 1011, 934, 886, 847, 754, 738, 639, 611 cm^{-1}; MS (MALDI-TOF): m/z (%): 269 (2) $[M+H]^+$, 268 (2) $[M]^+$; elemental analysis calcd (%) for $C_{21}H_{16}$ (268.3): C 94.02, H 5.97; found: C 93.87, H 6.09.

***syn*-9,10-Bis(2-ethylphenyl)anthracene (*syn*-3b)**: Yield: 380 mg (34%); R_f = 0.20 (hexane/ethyl acetate 50:1); m.p. 222°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.5 Hz, 6H; CH_3), 2.25 (q, J = 7.5 Hz, 4H; CH_2), 7.28–7.33 (m, 6H; 2-H, 3-H, 6-H, 7-H, 3-H Ar), 7.38–7.45 (m, 2H; 4-H Ar), 7.52–7.58 ppm (m, 7H; 1-H, 4-H, 5-H, 8-H, 5-H Ar, 6-H Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7 (q, CH_3), 26.3 (t, CH_2), 124.9 (d, C-2, C-3, C-6, C-7), 125.8 (d, C-4 Ar), 126.9 (d, C-1, C-4, C-6, C-8), 128.0, 128.2 (2 d, C-3 Ar, C-5 Ar), 129.9 (s, C-11, C-12, C-13, C-14), 131.5 (d, C-6 Ar), 136.2, 137.2, 143.8 ppm (3 s, C-9, C-10, C-1 Ar, C-2 Ar); IR (KBr): $\tilde{\nu}$ = 3058, 2965, 2931, 2870, 1488, 1438, 1386, 942, 752, 667 cm^{-1}; MS (MALDI-TOF): m/z (%): 387 (4) $[M+H]^+$.

***anti*-9,10-Bis(2-ethylphenyl)anthracene (*anti*-3b)**: Yield: 310 mg (29%); m.p. 297°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, J = 7.5 Hz, 6H; CH_3), 2.24 (q, J = 7.5 Hz, 4H; CH_2), 7.28–7.33 (m, 6H; 2-H, 3-H, 6-H, 7-H, 3-H Ar), 7.38–7.45 (m, 2H; 4-H Ar), 7.52–7.58 ppm (m, 8H; 1-H, 4-H, 5-H, 8-H, 5-H Ar, 6-H Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.9 (q, CH_3), 26.2 (t, CH_2), 125.0 (d, C-2, C-3, C-6, C-7), 125.7 (d, C-4 Ar), 126.9 (d, C-1, C-4, C-5, C-8), 128.0, 128.2 (2 d, C-3 Ar, C-5 Ar), 130.0 (s, C-11, C-12, C13, C-14), 131.5 (d, C-6 Ar), 136.2, 137.9, 143.8 ppm (3 s, C-9, C-10, C-1 Ar, C-2 Ar); IR (KBr): $\tilde{\nu}$ = 3053, 2964, 2930, 2868, 1486, 1439, 1387, 942, 771, 757, 668 cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{26}$ (386.3): C 93.22, H 6.78; found: C 92.98, H 6.90.

9-(2-Ethylphenyl)anthracene (4b): Yield: 107 mg (13%); R_f = 0.20 (hexane/ethyl acetate 50:1); m.p. 122°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.5 Hz, 3H; CH_3), 2.23 (q, J = 7.6 Hz, 2H; CH_2), 7.26–7.29 (m, 1H), 7.34–7.39 (m, 2H), 7.41–7.44 (m, 1H), 7.46–7.51 (m, 2H), 7.53–7.59 (m, 4H), 8.07 (d, J = 8.4 Hz, 2H; 4-H, 5-H), 8.53 ppm (s, 1H; 10-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.9 (q, Me), 26.3 (t, CH_2), 125.1, 125.3, 125.7, 126.3, 126.7, 128.1, 128.3, 128.4 (8 d, C-1, C-2, C-3, C-4, C-5, C-6, C-7, C-8, C-10, C-3 Ar, C-5 Ar), 130.3 (s, C-11, C-14), 131.3 (d, C-4 Ar), 131.4 (s, C-12, C-13), 136.3, 137.6, 143.7 ppm (3 s, C-9, C-1 Ar, C-2 Ar); IR (KBr): ν = 3051, 2963, 2870, 1442, 1355, 1010, 936, 889, 847, 752, 734, 640, 611 cm^{-1}; MS (MALDI-TOF): m/z (%): 283 (100) $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{18}$ (282.3): C 93.61, H 6.38; found: C 93.44, H 6.59.

***syn*-9,10-Bis(2-isopropylphenyl)anthracene (*syn*-3c)**: Yield: 408 mg (34%); R_f = 0.35 (hexane/ethyl acetate 1:50); m.p. 263°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (d, J = 6.8 Hz, 12H; CH_3), 2.51 (sept., J = 6.8 Hz, 2H; CH), 7.24 (dd, J = 7.5, 1.1 Hz, 2H; 3-H Ar), 7.29–7.32 (m, 6H; 2-H, 3-H, 6-H, 7-H, 4-H Ar), 7.38 (dt, J = 7.5, 1.6 Hz, 2H; 5-H Ar), 7.56–7.61 ppm (m, 6H; 1-H, 4-H, 5-H, 8-H, 6-H Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.2 (q, CH_3), 30.5 (d, CH), 124.9 (d, C-2, C-3, C-6, C-7), 125.6 (d, C-3 Ar, C-4 Ar), 127.1 (d, C-1, C-4, C-5, C-8), 128.3 (d, C-5 Ar), 130.2 (s, C-11, C-12, C-13, C14), 131.4 (d, C-6 Ar), 136.2, 137.3, 148.6 ppm (3 s, C-9, C-10, C-1 Ar, C-2 Ar); IR (KBr): $\tilde{\nu}$ = 3059, 2960, 2926, 2866, 1488, 1439, 1386, 1082, 1025, 944, 771, 668 cm^{-1}; MS (MALDI-TOF): m/z (%): 415 (1) $[M+H]^+$, 414 (2) $[M]^+$.

***anti*-9,10-Bis(2-isopropylphenyl)anthracene (*anti*-3c)**: Yield: 346 mg (29%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (d, J = 6.8 Hz, 12H; CH_3), 2.44 (sept., J = 6.9 Hz, 2H; CH), 7.17 (d, J = 7.5, 2H; 3-H Ar), 7.29–7.32 (m, 6H; 2-H, 3-H, 6-H, 7-H, 4-H Ar), 7.38 (dt, J = 7.5, 1.8 Hz, 2H; 5-H Ar), 7.55–7.59 ppm (m, 6H; 1-H, 4-H, 5-H, 8-H, 6-H Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.2 (q, CH_3), 30.4 (d, CH), 124.9 (d, C-2, C-3, C-6, C-7), 125.6, 125.7 (d, C-3 Ar, C-4 Ar), 127.1 (d, C-1, C-4, C-5, C-8), 128.3 (d, C-5 Ar), 130.1 (s, C-11, C-12, C-13, C14), 131.4 (d, C-6 Ar), 136.2, 137.2, 148.8 ppm (3 s, C-9, C-10, C-1 Ar, C-2 Ar); IR (KBr): ν = 3058, 2961, 2926, 2865, 1488, 1440, 1385, 1079, 1027, 944, 761, 667 cm^{-1}; elemental analysis calcd (%) for $C_{32}H_{30}$ (414.3): C 92.71, H 7.29; found: C 92.66, H 7.33.

9-(2-Isopropylphenyl)anthracene (4c): Yield: 217 mg (25%); R_f = 0.33 (hexane/ethyl acetate 10:1); m.p. 150°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98 (d, J = 6.8 Hz, 6H; Me), 2.51 (sept., J = 6.8 Hz, 1H; CH), 7.21 (d, J = 7.5 Hz, 1H), 7.31–7.39 (m, 3H), 7.46 (t, J = 6.6 Hz, 2H), 7.52–7.60 (m, 4H), 8.06 (d, J = 8.5 Hz, 2H; 4-H, 5-H), 8.51 ppm (s, 1H; 10-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.1 (q, Me), 30.4 (d, CH), 125.1, 125.2, 125.6, 126.3, 126.9, 128.3, 128.3 (7 d, C-1, C-2, C-3, C-4, C-5, C-6, C-7, C-8, C-10, C-3 Ar, C-5 Ar), 130.5 (s, C-10), 131.2, 131.4 (2 d, C-4 Ar, C-6 Ar), 136.4, 136.4, 136.9, 148.6 ppm (4 s, C-9, C-12, C-13, C-1 Ar, C-2 Ar); IR (KBr): ν = 3045, 2960, 2864, 1442, 1356, 1010, 937, 889, 847, 753, 734, 641, 611 cm^{-1}; MS (MALDI-TOF): m/z (%): 296 (2) $[M+H]^+$; elemental analysis calcd (%) for $C_{23}H_{20}$ (296.4): C 93.20, H 6.80; found: C 93.18, H 7.11.

***syn*-9,10-Bis(2-methoxyphenyl)anthracene (*syn*-3d)**: Yield: 405 mg (36%); R_f = 0.33 (hexane/ethyl acetate 10:1); m.p. 308°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67 (s, 6H; OMe), 7.18–7.24 (m, 4H), 7.32–7.36 (m, 4H; 2-H, 3-H, 6-H, 7-H), 7.57 (dt, J = 7.4, 1.8 Hz, 2H), 7.67–7.70 ppm (m, 4H; 1-H, 4-H, 5-H, 8-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\tilde{\delta}$ = 55.6 (q, OMe), 111.3 (d, C-3 Ar), 120.6 (d, C-4 Ar), 124.7 (d, C-2, C-3, C-6, C-7), 126.9 (d, C-1, C-4, C-5, C-8), 127.7 (s, C-11, C-12, C-13, C-14), 129.2, 130.1 (2 d, C-5 Ar, C-6 Ar), 133.0, 133.7 (2 s, C-9, C-10, C-1 Ar), 158.1 ppm (s, C-2 Ar); IR (KBr): $\tilde{\nu}$ = 3059, 2933, 2833, 1597, 1577, 1494, 1459, 1432, 1274, 1243, 1106, 1046, 1022, 942, 752, 665 cm^{-1}; MS (MALDI-TOF): m/z (%): 391 (100) $[M+H]^+$, 390 (77) $[M]^+$, 375 (15) $[M-CH_3]^+$.

***anti*-9,10-Bis(2-methoxyphenyl)anthracene (*anti*-3d)**: Yield: 496 mg (44%); m.p. 318°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.66 (s, 6H; OMe), 7.18–7.24 (m, 4H), 7.32–7.36 (m, 4H; 2-H, 3-H, 6-H, 7-H), 7.57 (dt, J = 7.4, 1.8 Hz, 2H; 5-H Ar), 7.67–7.70 ppm (m, 4H; 1-H, 4-H, 5-H, 8-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.6 (q, OMe), 111.3 (d, C-3 Ar), 120.6 (d, C-4 Ar), 124.7 (d, C-2, C-3, C-6, C-7), 126.9 (d, C-1, C-4, C-5, C-8), 127.7 (s, C-11, C-12, C-13, C-14), 129.2, 130.1 (2 d, C-5 Ar, C-6 Ar), 133.0, 133.7 (2 s, C-9, C-10, C-1 Ar), 158.1 ppm (s, C-2 Ar); IR (KBr): $\tilde{\nu}$ = 3024, 2931, 2834, 1596, 1576, 1491, 1459, 1431, 1291, 1277, 1240, 1104, 1046, 1019, 942, 752, 665 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{22}O_2$ (390.2): C 86.13, H 5.68; found: C 85.73, H 5.51.

***syn*- and *anti*-9,10-Bis(2-fluorophenyl)anthracene (*syn*- and *anti*-3e)**: Yield: 785 mg as a mixture of the two isomers (74%) by the thermal procedure; 944 mg (90%) under microwave conditions; R_f = 0.3 (hexane/ethyl acetate 50:1); m.p. 265°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.42 (m, 4H; 2-H, 3-H, 6-H, 7-H), 7.44–7.51 (m, 2H), 7.54–7.62 (m, 2H), 7.66–7.70 ppm (m, 4H; 1-H, 4-H, 5-H, 8-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 115.9 (d, $J_{C,F}$ = 22.2 Hz, C-3 Ar), 124.2 (d, $J_{C,F}$ = 3.8 Hz, C-5 Ar), 125.5 (d, C-2, C-3, C-6, C-7), 126.1 (s, $J_{C,F}$ = 17.5 Hz, C-1 Ar), 126.5 (d, C-1, C-4, C-5, C-8), 129.9 (d, $J_{C,F}$ = 7.6 Hz, C-4 Ar), 130.1 (s, C-11, C-12, C-13, C-14), 131.1 (s, C-9, C-10), 131.2 (s, C-9, C-10), 133.4 (d, $J_{C,F}$ = 3.5 Hz, C-6 Ar), 160.8 ppm (s, $J_{C,F}$ = 246 Hz, C-16); ^{19}F NMR (282.4 MHz, $CDCl_3$ + $CFCl_3$) = −113.15 (m, 2F, *syn*-**1e**), −114.1 ppm (m, 2F, *anti*-**1e**); $\tilde{\nu}$ = 2962, 1490, 1447, 1387, 1262, 1223, 1094, 1028, 944, 817, 756 cm^{-1}; MS (MALDI-TOF): m/z (%): 367 (6) $[M+H]^+$, 366 (20) $[M]^+$; elemental analysis calcd (%) for $C_{26}H_{16}F_2$ (366.7): C 85.29, H 4.37; found: C 85.78, H 3.88.

***syn*-9,10-Bis(2-cyanophenyl)anthracene (*syn*-3f)**: Instead of 2-cyanophenylboronic acid (**2f**), 2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzonitrile (3.18 g, 5 equiv, 14.7 mmol) was used. Yield: 290 mg (26%); R_f = 0.31 (hexane/ethyl acetate 3:1); m.p. 315°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.46 (m, 4H; 2-H, 3-H, 6-H, 7-H), 7.50–7.56 (m, 4H; 1-H, 4-H, 5-H, 8-H), 7.59 (d, J = 7.7 Hz, 2H; 6-H Ar), 7.70 (dd, J = 7.6 Hz, 7.7 Hz, 2H; 4-H Ar), 7.85 (dd, J = 7.6 Hz, 7.7 Hz, 2H; 5-H Ar), 7.99 ppm (d, J = 7.6 Hz, 2H; 3-H Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 115.8 (s, C-2 Ar), 117.5 (s, CN), 126.4 (d, C-2, C-3, C-6, C-7), 126.6 (d, C-1, C-4, C-5, C-8), 128.9 (d, C-6 Ar), 130.2 (s, C-11, C-12, C-13, C-14), 132.8 (d, C-4 Ar),

132.9 (d, C-5 Ar), 133.7 (d, C-3 Ar), 134.2 (s, C-10), 143.1 ppm (s, C-1 Ar); IR (KBr): $\tilde{\nu}$ = 3060, 2226, 1593, 1478, 1437, 1380, 1184, 1025, 939, 751 cm^{-1}; MS (MALDI-TOF): *m*/*z* (%): 381 (14) $[M+H]^+$, 279 (20) $[M-ArCN]^+$.

***anti*-9,10-Bis(2-cyanophenyl)anthracene (*anti*-3f)**: Yield: 312 mg (28%); m.p. >350°C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.44 (m, 4H; 2-H, 3-H, 6-H, 7-H), 7.46–7.52 m, 4H; 1-H, 4-H, 5-H, 8-H), 7.65–7.74 (m, 4H; 4-H Ar, 6-H Ar), 7.88 (dd, *J* = 7.6, 7.7 Hz, 2H; 5-H Ar), 7.99 ppm (d, *J* = 7.6 Hz, 2H; 3-H Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 115.8 (s, C-2 Ar), 117.4 (s, CN), 126.4 (d, C-2, C-3, C-6, C-7), 126.6 (d, C-1, C-4, C-5, C-8), 128.8 (d, C-6 Ar), 130.2 (s, C-11, C-12, C-13, C-14), 132.8 (d, C-4 Ar), 132.9 (d, C-5 Ar), 133.7 (d, C-3 Ar), 134.2 (s, C-10), 143.0 ppm (s, C-1 Ar); IR (KBr): $\tilde{\nu}$ = 3056, 2230, 1593, 1486, 1437, 1384, 1086, 1021, 947, 758 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{16}N_2$ (380.3): C 88.42, H 4.21, N 7.36; found: C 88.01, H 4.22, N 7.32.

9-(2-Cyanophenyl)anthracene (4f): Yield: 262 mg (32%); R_f = 0.31 (hexane/ethyl acetate 3:1); m.p. 190°C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.52 (m, 6H), 7.56 (d, *J* = 7.6 Hz, 1H; 6-H Ar), 7.6 (dd, *J* = 7.6, 7.7 Hz, 1H; 5-H Ar), 7.82 (dd, *J* = 7.6, 7.7 Hz, 1H; 4-H Ar), 7.96 (d, *J* = 7.7 Hz, 2H; 3-H Ar), 8.10 (d, *J* = 8.3 Hz, 2H; 4-H, 5-H), 8.60 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 115.5 (s, C-2 Ar), 117.9 (s, CN), 125.6 (d, C-2, C-7), 125.8 (d, C-3, C-6), 126.7 (C-1, C-4, C-5, C-8), 128.6, 128.7 (d, C-6 Ar), 129.1, 130.5 (s, C-10), 131.6 (s, C-9), 132.9, 133.0, 133.5, 143.0 ppm (s, C-1 Ar); MS (MALDI-TOF): *m*/*z* (%): 281 (43) $[M+H]^+$, 280 (7) $[M]^+$.

***syn*- and *anti*-9,10-Bis(2-formylphenyl)anthracene (*syn*- and *anti*-3g)**: Yield of a mixture of the two isomers: 851 mg (75%); R_f = 0.24 (hexane/ethyl acetate 10:1); m.p. 300°C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.40 (m, 4H; 2-H, 3-H, 6-H, 7-H), 7.50–7.55 (m, 6H; 1-H, 4-H, 5-H, 8-H, 6-H Ar), 7.75 (t, *J* = 7.5 Hz, 2H; 4-H Ar), 7.85 (dt, *J* = 7.4, 1.5 Hz, 1H; 5-H Ar), 7.86 (dt, *J* = 7.4, 1.5 Hz, 1H; 5-H Ar), 8.23 (d, *J* = 7.7 Hz, 2H; 3-H Ar), 8.27 (d, *J* = 7.7 Hz, 2H; 3-H Ar), 9.39 (d, *J* = 0.7 Hz, 1H; CHO), 9.42 ppm (d, *J* = 0.6 Hz, 1H; CHO); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 126.2, 126.2 (2 d, C-3 Ar), 126.6 (d, C-3, C-4, C-6, C-7), 127.4 (d, C-4 Ar), 128.8 (d, C-1, C-4, C-5, C-8), 130.5 (s, C-11, C-12, C-13, C-14), 132.5, 132.7 (2 d, C-5 Ar), 132.9 (s, C-9, C-10), 134.1, 134.2 (2 d, C-6 Ar), 135.7, 142.5, 142.6 (3 s, C-1 Ar, C-2 Ar), 191.4, 191.7 ppm (2 d, CHO); IR (KBr): $\tilde{\nu}$ = 3059, 2827, 2738, 1694, 1595, 1438, 1380, 1266, 1201, 1094, 942, 824, 667 cm^{-1}; MS (MALDI-TOF): *m*/*z* (%): 387 (3) $[M+H]^+$; elemental analysis calcd (%) for $C_{28}H_{18}O_2$ (386.43): C 87.03, H 4.69; found: C 86.85, H 4.90.

***syn*-9,10-Bis(2-fluoro-5-methoxyphenyl)anthracene (*syn*-3h)**: Yield: 788 mg (63%) as a mixture with *anti*-**3h**; ^1H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 6H; OMe), 6.97 (dd, *J* = 5.56, 3.11 Hz, 2H; 6-H Ar), 7.09 (ddd, *J* = 8.85, 3.11, 5.75 Hz, 2H; 4-H Ar), 7.29 (dd, *J* = 8.85, 8.76 Hz, 2H; 3-H Ar), 7.41–7.44 (m, 4H; 2-H, 3-H, 6-H, 7-H), 7.75–7.78 ppm (m, 4H; 1-H, 4-H, 5-H, 8-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.3 (q, OMe), 115.9 (d, *J* = 7.68 Hz, C-4 Ar), 116.8 (d, *J* = 24.15 Hz, C-3 Ar), 117.9 (d, *J* = 3.29 Hz, C-6 Ar), 125.9, 125.9, 126.0, 126.1 (d, C-2, C-3, C-6, C-7), 126.9 (s, *J* = 19.49 Hz, C-1 Ar), 126.86, 126.87, 126.8 (2 s, C-1, C-4, C-5, C-8), 130.3, 130.3, 130.8, 130.3 (s, C-11, C-12, C-13, C-14), 131.5, 131.5 (s, C-9, C-10), 155.6 (s, *J* = 238.49 Hz, C-2 Ar), 156.1 ppm (s, *J* = 2.17 Hz, C-5 Ar); ^{19}F NMR (282.4 MHz, $CDCl_3+CFCl_3$): δ = −125.1 ppm; MS (MALDI-TOF): *m*/*z* (%): 426 (5) $[M]^+$.

***anti*-9,10-Bis(2-fluoro-5-methoxyphenyl)anthracene (*anti*-3h)**: Yield: 268 mg (43%) under microwave conditions; m.p. 275°C; ^1H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 6H; OMe), 6.98 (dd, *J* = 3.11, 5.65 Hz, 2H; 6-H Ar), 7.09 (ddd, *J* = 3.11, 8.85, 5.65 Hz, 2H; 4-H Ar), 7.26 (dd, *J* = 8.85, 8.67 Hz, 2H; 3-H Ar), 7.38–7.41 (m, 4H; 2-H, 3-H, 9-H, 10-H), 7.70–7.74 ppm (m, 4H; 1-H, 4-H, 5-H, 8-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.3 (q, OMe), 115.9 (d, $^3J_{C,F}$ = 7.68 Hz, C-4 Ar), 116.8 (d, $^2J_{C,F}$ = 24.15 Hz, C-3 Ar), 117.9 (d, $^3J_{C,F}$ = 3.57 Hz, C-6 Ar), 125.9, 126.0, (4 d, C-2, C-3, C-6, C-7), 126.9 (s, $^2J_{C,F}$ = 19.21 Hz, C-11), 126.8, (4 d, C-1, C-4, C-5, C-8), 130.3, 130.40 (4 s, C-11, C-12, C-13, C-14), 131.56, 131.57 (s, C-9, C-10), 155.6 (s, $^1J_{C,F}$ = 238.49 Hz, C-2 Ar), 156.1 ppm (s, $^4J_{C,F}$ = 2.20 Hz, C-5 Ar); ^{19}F NMR (282.4 MHz, $CDCl_3+CFCl_3$): δ = −125.3 ppm; HRMS (ESI): *m*/*z*: calcd for $C_{28}H_{20}F_2O_2$: 426.1431 $[M]^+$; found 426.1418.

Thermal isomerisation: Kinetic studies were carried out with *anti*-**3h** (20 mg) in $C_2D_2Cl_4$. The solution was heated at 70°C for a certain time, rapidly cooled to room temperature and a ^{19}F NMR spectrum was recorded. Compounds *syn*- and *syn*-**3d** were heated neat in the solid state in an oven at 320°C for 10 min. After rapid cooling, the solid was dissolved in $CDCl_3$ and a ^1H NMR spectrum was recorded.

Sensitised photo-oxidation of the anthracenes: The photo-oxidation reactions were carried out in 20 mL glass tubes in which the anthracene (1 mmol for the *syn* isomers and 0.2 mmol for the *anti* isomers) and a catalytic amount of methylene blue were dissolved in $CDCl_3$ (6 mL). The tube was sealed with a rubber stopper and cooled to −20°C. A slow constant stream of oxygen was bubbled into the solution through a needle while the cooled tube was irradiated with two sodium lamps (200 W). The photo-oxidation reactions were monitored by TLC and stopped after complete consumption of the starting material. The solvents were removed under vacuum at room temperature and the crude products were purified by column chromatography.

Chemical ("dark") oxygenation of 3e in microemulsions: The emulsion was prepared by mixing sodium dodecylsulfate (770 mg, 2.67 mmol) with *n*-butanol (1 mL) and dichloromethane (5 mL). A solution of sodium molybdate (120 mg, 0.5 mmol) in water (0.5 mL) was added dropwise and the emulsion was mixed until the liquid became transparent. This emulsion solution was then added to anthracene **3e** (98 mg, 0.27 mmol), which completely dissolved. Singlet oxygen was generated after addition of H_2O_2 (30%, 10 μL), which caused the colour of the solution to turn red-brown. The colour faded to yellow after 10–15 min, which indicated the depletion of singlet oxygen. Another 20 portions of H_2O_2 were added in the same way until, finally, the liquid became heterogeneous. Then the solvent was evaporated and dichloromethane (5 mL) was added to the residue. After filtration the solvent was evaporated and the residue, which contained the starting material **3e** and the reaction product, was again treated with the emulsion solution as described above. Complete conversion from **3e** to **5e** was attained after five or six cycles.

9,10-Bis(2-methylphenyl)-9,10-dihydro-9,10-epidioxyanthracene (5a): Yield: 331 mg (85%) from *syn*-**3a** and 38 mg (49%) from *anti*-**3a**; R_f = 0.44 (hexane/ethyl acetate (EA) 10:1); ^1H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 6H; CH_3), 7.08–7.05 (m, 4H; 2-H, 3-H, 6-H, 7-H), 7.22–7.25 (m, 4H; 1-H, 4-H, 5-H, 8-H), 7.38–7.52 (m, 6H; 3-H Ar, 4-H Ar, 5-H Ar), 7.73 ppm (d, *J* = 7.2 Hz, 2H; 6-H Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.9 (q, CH_3), 84.0 (s, C-9, C-10), 124.2 (d, C-2, C-3, C-6, C-7), 126.3, 126.7 (2 d, C-3 Ar, C-4 Ar), 127.8 (d, C-1, C-4, C-5, C-8), 128.3, 131.3 (2 d, C-5 Ar, C-6 Ar), 133.0, 135.6, 137.7 ppm (3 s, C-11, C-12, C-13, C-14, C-1 Ar, C-2 Ar); IR (KBr): $\tilde{\nu}$ = 3059, 2920, 1491, 1458, 1437, 1383, 1246, 1024, 942, 767, 751, 666 cm^{-1}; MS (MALDI-TOF): *m*/*z* (%): 391 (17) $[M+H]^+$, 390 (61) $[M]^+$, 375 (9) $[M-CH_3]^+$; elemental analysis calcd (%) for $C_{28}H_{22}O_2$ (390.2): C 86.13, H 5.68; found: C 85.81, H 5.82.

9,10-Bis(2-methylphenyl)-1,4-dihydro-1,4-epidioxyanthracene (6a): Not isolated; R_f = 0.24 (hexane/EA 10:1); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.98 (s, 3H; 21-H), 2.11 (s, 3H; 22-H), 5.34 (ddd, *J* = 4.5, 3.0, 0.7 Hz, 1H; 1-H), 5.40 (ddd, *J* = 4.6, 2.9, 0.7 Hz, 1H; 4-H), 6.91–6.96 (m, 2H; 2-H, 3-H), 7.19 (d, *J* = 7.1 Hz, 1H), 7.31–7.51 ppm (m, 11H).

9,10-Bis(2-ethylphenyl)-9,10-dihydro-9,10-epidioxyanthracene (5b): Yield: 221 mg (53%) from *syn*-**3b** and 22 mg (27%) from *anti*-**3b**; R_f = 0.6 (hexane/EA 10:1); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.5 Hz, 6H; CH_3), 2.53 (q, *J* = 7.5 Hz, 4H; CH_2), 7.07–7.10 (m, 4H; 2-H, 3-H, 6-H, 7-H), 7.24–7.27 (m, 4H; 1-H, 4-H, 5-H, 8-H), 7.43 (t, *J* = 8.4 Hz, 2H; 4-H Ar), 7.55 (dt, *J* = 7.5, 1.3 Hz, 2H; 5-H Ar), 7.69 (d, *J* = 7.3 Hz, 2H; 3-H Ar), 7.73 ppm (dd, *J* = 7.9, 1.1 Hz, 2H; 6-H Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (q, C-CH_3), 27.3 (t, CH_2), 84.1 (s, C-9, C-10), 124.1 (d, C-2, C-3, C-6, C-7), 125.9, 126.7 (2 d, C-3 Ar, C-4 Ar), 127.7 (d, C-1, C-4, C-5, C-8), 128.4, 128.5 (2 d, C-5 Ar, C-6 Ar), 132.3, 137.9, 141.3 ppm (3 s, C-11, C-12, C-13, C-14, C-1 Ar, C-2 Ar); HRMS (TOF EI+): *m*/*z*: calcd for $C_{30}H_{26}O_2$: 418.1933 $[M]^+$; found 418.1932; calcd for $C_{30}H_{26}$: 386.2035 $[M-O_2]^+$; found 386.2027.

9,10-Bis(2-ethylphenyl)-1,4-dihydro-1,4-epidioxyanthracene (6b): Yield: 22 mg (27%) from *anti*-**3b**; R_f = 0.5 (hexane/EA 10:1); ^1H NMR (300 MHz, $CDCl_3$): δ = 0.97 (t, *J* = 7.5 Hz, 3H; CH_3), 1.05 (t, *J* = 7.5 Hz, 3H; CH_3'), 2.29 (q, *J* = 7.5 Hz, 1H; CH_2), 2.31 (q, *J* = 7.5 Hz, 1H; CH_2),

2.44 (q, $J=7.5$ Hz, 2H; CH_2'), 5.36 (ddd, $J=5.0$, 2.5, 1.0 Hz, 1H; 1-H), 5.41 (ddd, $J=5.1$, 2.4, 0.9 Hz, 1H; 4-H), 6.89–6.95 (m, 2H; 3-H, 4-H), 7.18 (d, $J=7.3$ Hz, 1H), 7.31–7.48 ppm (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=14.9$, 15.4 (2 q, CH_3), 26.3 (t, CH_2), 73.7, 73.9 (2 s, C-1, C-4), 125.6, 126.0, 126.2, 126.8, 126.9 (5 d), 128.3, 128.4, 128.4, 128.5 (4 d), 130.9, 131.0 (2 d), 131.5, 131.6, 132.4, 132.7, 132.8 (5 s), 135.1, 135.2, 135.3, 135.5 (4 d, C-2, C-3), 143.5, 143.8 ppm (2 s, C-2 Ar); HRMS (ESI): m/z: calcd for $C_{30}H_{26}O_2$: 419.2005 $[M+H]^+$; found 419.2004.

9,10-Bis(2-isopropylphenyl)-9,10-dihydro-9,10-epidioxyanthracene (5c): Isolation from *syn*- and *anti*-**3c** in the crude product mixture was impossible. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.70$ (d, $J=6.9$ Hz, 12H; CH_3), 2.05–2.20 (m, 2H; CH), 6.85–6.95 (m, 4H; 2-H, 3-H, 6-H, 7-H), 7.18–7.26 (m, 6H; 1-H, 4-H, 5-H, 8-H, 3-H Ar), 7.30–7.60 ppm (br, 3H).

9,10-Bis(2-isopropylphenyl)-1,4-dihydro-1,4-epidioxyanthracene (6c): Yield: 14 mg (16%) from *anti*-**3c**; not isolated; $R_f=0.39$ (hexane/ethyl acetate 20:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.65$ (d, $J=6.8$ Hz, 12H; CH_3), 2.54 (sept., $J=6.8$ Hz, 1H; CH), 2.75 (sept., $J=6.7$ Hz, CH), 5.36 (ddd, $J=5.5$, 1.7, 1.0 Hz, 1H), 5.41 (ddd, $J=5.3$, 1.7, 0.9 Hz, 1H), 6.91 (ddd, $J=7.9$, 5.5, 1.7 Hz, 2H), 7.16 (dd, $J=7.4$, 0.8 Hz, 1H), 7.29–7.59 ppm (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=23.8$, 24.2 (2 q, CH_3), 30.0, 30.2 (2 d, CH_2), 73.7, 73.9 (2 d, C-1, C-4), 124.8, 125.5, 125.5, 125.9, 125.9, 126.2, 126.9, 127.0 (8 d), 128.6, 128.7 (2 d), 130.8, 130.8, 131.7 (3 d), 131.8, 132.6, 132.7, 132.8, 134.5 (5 s), 135.2, 135.4 (2 d, C-2, C-3), 148.3, 148.7 ppm (2 s, C-2 Ar); HRMS (TOF EI+): m/z: calcd for $C_{32}H_{30}O_2$: 446.2246 $[M]^+$; found 446.2267; $C_{32}H_{30}$: 414.2340 $[M-O_2]^+$; found 414.2330.

9,10-Bis(2-methoxyphenyl)-9,10-dihydro-9,10-epidioxyanthracene (5d): Yield: 337 mg (80%) from *syn*-**3d** and 51 mg (61%) from *anti*-**3d**; $R_f=0.5$ (hexane/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=3.75$ (s, 6H; OMe), 6.96–6.99 (m, 4H; 2-H, 3-H, 6-H, 7-H), 7.15–7.18 (m, 4H; 1-H, 4-H, 5-H, 8-H), 7.21 (d, $J=7.6$ Hz, 4H), 7.55 (dt, $J=7.5$, 1.7 Hz, 2H), 7.73 ppm (dd, $J=7.4$, 1.1 Hz, 2H; 6-H Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=55.0$ (q, OMe), 83.4 (s, C-9, C-10), 111.0 (d, C-3 Ar), 121.5 (d), 122.9 (s, C-1 Ar), 123.6 (d, C-2, C-3, C-6, C-7), 126.8 (d, C-1, C-4, C-5, C-8), 127.4 (d), 129.7 (d), 137.7 (s, C-11, C-12, C-13, C-14), 156.2 ppm (s, C-2 Ar); IR (KBr): $\tilde{\nu}=3071$, 2936, 2835, 1602, 1583, 1493, 1461, 1435, 1266, 1245, 1025, 910, 754, 662, 639 cm^{-1}; MS (MALDI-TOF): m/z (%): 423 (63) $[M+H]^+$, 390 (19) $[M-O_2]^+$, 375 (19) $[M-O_2-CH_3]^+$; elemental analysis calcd (%) for $C_{28}H_{22}O_4$ (422.3): C 79.62, H 5.21; found: C 79.61, H 5.34.

9,10-Bis(2-fluorophenyl)-9,10-dihydro-9,10-epidioxyanthracene (5e): Yield: 370 mg (93%) from a mixture of *syn* and *anti*-**3e**; $R_f=0.5$ (hexane/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.09$–7.14 (m, 4H), 7.26–7.29 (m, 4H), 7.39–7.45 (m, 4H), 7.57–7.65 (m, 2H), 7.75–7.81 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=82.8$ (s, $J_{C,F}=1.9$ Hz, C-9, C-10), 115.9 (d, $J_{C,F}=21.1$ Hz, C-3 Ar), 121.6 (s, $J_{C,F}=13.7$ Hz, C-1 Ar), 123.1 (d, $J_{C,F}=3.0$ Hz, C-2, C-3, C-6, C-7), 125.3 (d, $J_{C,F}=3.0$ Hz, C-5 Ar), 127.6 (d, $J_{C,F}=3.0$ Hz, C-6 Ar), 127.9 (d, C-1, C-4, C-5, C-8), 130.6 (d, $J_{C,F}=7.9$ Hz, C-4 Ar), 137.5 (s, C-11, C-12, C-13, C-14), 158.8 ppm (s, $J_{C,F}=248$ Hz, C-2 Ar); ^{19}F NMR (282.4 MHz, $CDCl_3$) $=-105.27$ ppm (m, 2 F). IR (KBr): $\tilde{\nu}=3071$, 3070, 3038, 1618, 1579, 1493, 1457, 1322, 1218, 912, 758, 638 cm^{-1}; MS (MALDI-TOF): m/z (%): 399 (100) $[M+H]^+$, 366 (77) $[M-O_2]^+$; elemental analysis calcd (%) for $C_{26}H_{16}F_2O_2$ (398.6): C 78.43, H 4.02; found: C 78.24, H 3.46.

9,10-Bis(2-cyanophenyl)-9,10-dihydro-9,10-epidioxyanthracene (5f): Yield: 231 mg (56%) from *syn*-**3f** and 30 mg (37%) from *anti*-**3f**; $R_f=0.28$ (cyclohexane/EA 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.12$–7.16 (m, 4H; 2-H, 3-H, 6-H, 7-H), 7.32–7.38 (m, 4H; 1-H, 4-H, 5-H, 8-H), 7.67–7.73 (m, 2H; 4-H Ar), 7.84–7.89 (m, 2H; 5-H Ar), 7.95 (d, $J=7.7$ Hz, 2H; 6-H Ar), 8.05 ppm (d, $J=7.7$ Hz, 2H; 3-H Ar); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=84.5$ (s, C-9, C-10), 113.2 (s, C-2 Ar), 118.1 (s, CN), 124.0 (d, C-2, C-3, C-7, C-8), 126.4 (s, C-4 Ar), 127.8 (d, C-3 Ar), 128.8 (d, C-1, C-4, C-5, C-8), 129.4 (d, C-6 Ar), 134.1 (d, C-5 Ar), 134.5 (d, C-1 Ar), 137.2 ppm (s, C-11, C-12, C-13, C-14); HRMS (ESI+): m/z: calcd for $C_{28}H_{16}N_2O_2$: 414.1344; found: 414.1353.

9,10-Bis(2-formyphenyl)-9,10-dihydro-9,10-epidioxyanthracene (5g): Photo-oxygenation of the isomeric mixture of **3g** afforded no endoperoxide.

9,10-Bis(2-fluoro-5-methoxyphenyl)-9,10-dihydro-9,10-epidioxyanthracene (5h): Yield: 339 mg (75%) from *anti*-**3h**; $R_f=0.27$ (cyclohexane/EA 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=3.85$ (s, 6H; OMe), 7.07–7.17 (m, 6H; 3-H Ar, 4-H Ar, 6-H Ar), 7.26–7.37 ppm (m, 8H; 1-H, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=56.3$ (q, OMe), 82.5 (s, C-9, C-10), 112.1 (d, $^3J_{C,F}=3.29$ Hz, C-6 Ar), 116.8 (d, $^3J_{C,F}=7.96$ Hz, C-4 Ar), 117.1 (d, $^2J_{C,F}=23.37$ Hz, C-3 Ar), 122.5 (s, $^2J_{C,F}=15.37$ Hz, C-11), 123.56, 123.57, 123.58, 123.59 (d, C-2, C-3, C-6, C-7), 123.60, 123.61, 123.62, 123.63 (d, C-1, C-4, C-5, C-8), 128.38, 128.39, 128.40, 128.41 (s, C-1, C-4, C-5, C-8), 137.81, 137.82, 137.83, 137.84 (s, C-10, C-11, C-12, C-13), 153.4 (s, $^1J_{C,F}=240.98$ Hz, C-1 Ar), 157.0 ppm (s, $^4J_{C,F}=1.67$ Hz, C-5 Ar); ^{19}F NMR: $\delta=-116.3$ ppm; HRMS (ESI+): m/z: calcd for $C_{28}H_{20}F_2O_2$: 459.1408; found: 459.1391.

Photolysis of the endoperoxide 5e: A solution of the endoperoxide **5e** (50 mg, 0.1 mmol) in acetonitrile (5 mL) was transferred into a quartz tube and irradiated for 48 h in a Rayonet reactor chamber at a wavelength of 254 nm at room temperature. The course of the reaction was monitored by TLC, which indicated the formation of the parent anthracene and several byproducts. After evaporation of the solvent a ^{19}F NMR spectrum was recorded in $CDCl_3$. ^{19}F NMR: $\delta=-104.2$, -105.2 (**5e**), -108.1, -109.9, -110.6, -113.1 ppm (*syn*-**3e**).

Acknowledgements

We thank Daniela Boden for her synthetic contribution and the group of Prof. Kleinpeter for conducting all NMR spectroscopy experiments. Generous financial support from the Deutsche Forschungsgemeinschaft (DFG, Li 556/9-1) is acknowledged.

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Received: July 4, 2008
Published online: November 12, 2008

