Palladium-Catalyzed Self-Cross Coupling of *o*-Bromo-*trans*-stilbenes To Yield 9,10-Bis(arylmethylene)-9,10-dihydroanthracenes☆

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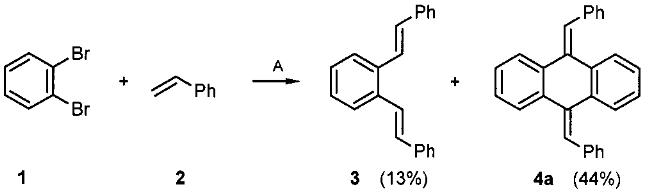
Under Palladium catalysis [Pd(OAc)$_2$, K$_2$CO$_3$, LiCl, Bu$_4$NBr, DMF] *o*-bromo-*trans*-stilbene (*trans*-**7a**) reacts to give 9,10-dibenzylidene-9,10-dihydroanthracene (**4a**) with formation of a new six-membered ring. The (*Z*) diastereomer crystallizes preferentially to give pure (*Z*)-**4a**, as proved by X-ray crystal structure analysis. A variety of substituted *o*-bromostilbenes and heterocyclic analogs **7** were prepared by Wittig olefination of *o*-bromobenzaldehyde with substituted benzyltriphenylphosphonium ylides, Wittig-Horner-Emmons olefination of arenecarbaldehydes with diethyl *o*-bromobenzylphosphonate or Wittig olefination of substituted benzaldehydes with substituted (*o*-bromobenzyl)diphenylphosphonium ylides, respectively. The *cis*-*o*-bromostilbenes were photoisomerized to the *trans* diastereoisomers *trans*-**7** by irradiation in the presence of diphenyl disulfide. All of these *o*-bromo-*trans*-stilbenes *trans*-**7a**–**g** and *trans*-**7j**, **k** under palladium catalysis reacted to the corresponding 9,10-bis(arylmethylene)-9,10-dihydroanthracenes **4**, mostly as mixtures of (*E*) and (*Z*) diastereomers (50–97 % yield). The (*Z*) diastereomer of the parent **4a** and the alkyl-substituted compounds **4c** and **4e** could be purified by simple crystallization, and in some runs, only (*Z*)-**4a**, **c**, **e** were obtained. Among the heterocyclic analogs *trans*-**7h**, **i** only the furyl derivative *trans*-**7h** reacted (76 % yield) cleanly, whereas the pyridine analog *trans*-**7i** gave a mixture of products from which the rather sensitive product **4i** could not be isolated in pure form. The *cis*-*o*-bromostilbenes *cis*-**7a**, **c** cyclized to phenanthrenes under the same conditions (70–71 % yield). The UV spectra of compounds **4a**, **c**–**k** are similar to that of anthracene, and so are the oxidation and reduction potentials of (*Z*)-**4a**.

Introduction

The palladium-catalyzed coupling of aryl and alkenyl halides with alkenes, the so-called Heck reaction[1], has become a major tool for C−C bond formation in organic synthesis[2][3]. It is a straightforward method for the preparation of styrenes, stilbenes, dienes, trienes, and a great variety of bi-, tri-, and oligocyclic systems derived therefrom[3]. A number of different conditions have been developed, and several unusual neighboring group involvements have been observed[4]. Incidentally, we came across an efficient self-cross coupling of *o*-bromo-*trans*-stilbene, and were able to show that it is reasonably general for substituted *o*-bromo-*trans*-stilbenes as well.

In the presence of an excess of styrene (**2**), *o*-dibromobenzene (**1**) gives a very high yield (92%) of *o*-distyrylbenzene (**3**)[5], when an appropriate palladium catalyst system[6] is used[7]. However, in an attempt to prepare *o*-bromo-*trans*-stilbene (*trans*-**7a**) by a single coupling of **1** and styrene **2** under the conditions of Jeffery[6], starting with a 1:1 mixture of the two, a new product was obtained as the predominant one (44%) besides **3** (13%) and some *trans*-stilbene (3%) resulting from reductive debromination of the intermediate *trans*-**7a** (Scheme 1).

Scheme 1. A: Pd(OAc)$_2$, K$_2$CO$_3$, LiCl, *n*Bu$_4$NBr, DMF, 110°C, 18 h



The ^{1}H- and ^{13}C-NMR spectra together with the elemental analysis data disclosed the new product as 9,10-bis(phenylmethylene)-9,10-dihydroanthracene (**4a**), a compound which had previously been prepared by dehydration of 9-(phenylmethylene)-9,10-dihydro-10-anthranol[8] and by twofold Wittig olefination of anthraquinone[9]. The assigned (*E*) configuration of the latter product on the basis of the NMR data alone[9], however, did not appear to be fully justified, and since the spectral data of the product

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[∓] X-ray crystal structure analyses.

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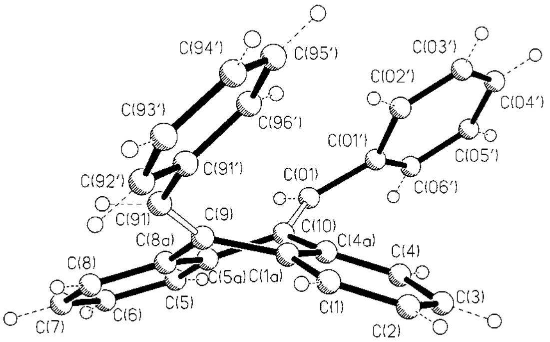
obtained from **1** and **2** were identical, an X-ray structure analysis was carried out with the pale yellow needles of **4a**, which crystallized from CH_2Cl_2/EtOH (10:1). This established the crystalline **4a** as the (*Z*)-configurated compound (Figure 1)[10].

Figure 1. Structure of (*Z*)-9,10-bis(phenylmethylene)-9,10-dihydroanthracene [(*Z*)-**4a**] in the crystal



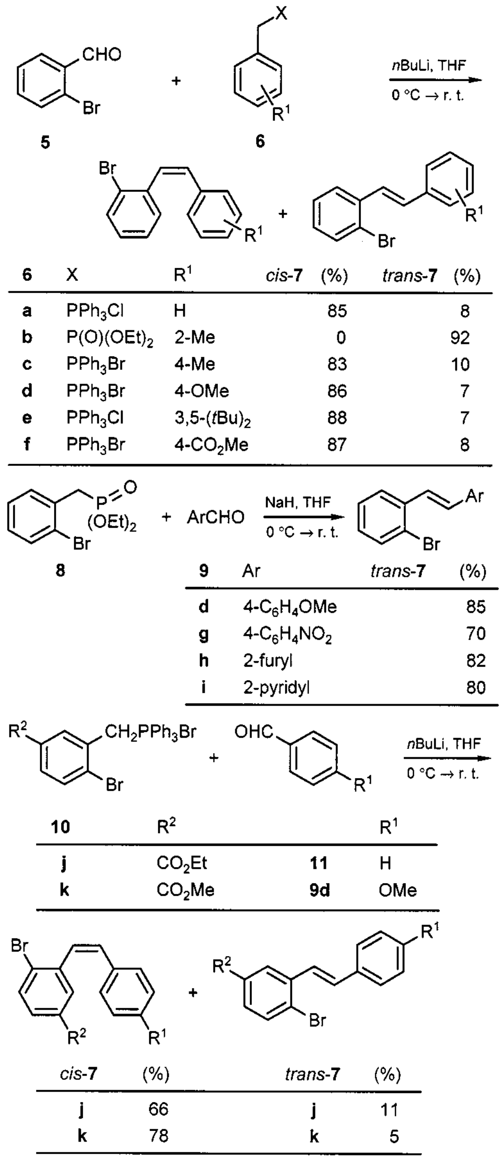
Preparation of *o*-Bromostilbenes and Their Palladium-Catalyzed Transformations

A control experiment, in which a 1:1 mixture of *o*-distyrylbenzene (**3**) and *o*-dibromobenzene (**1**) was subjected to the same conditions, readily disclosed that **4a** was not formed by further coupling of **3** with **1**, but must have arisen from self-cross coupling of *o*-bromo-*trans*-stilbene (**7a**). To prove this and to also test the scope and limitations of this new ring-forming reaction, authentic **7a**[11] as well as several substituted analogs **7b**–**k** were prepared.

The Wittig olefination of *o*-bromobenzaldehyde with benzyltriphenylphosphonium chloride (**6a**) gave a mixture of mainly *o*-bromo-*cis*-stilbene (*cis*-**7a**) (85%) and a little *trans*-**7a** (8%). Similar yields and ratios of *cis*- and *trans*-stilbenes **7c**–**f** were obtained with the substituted benzyltriphenylphosphonium halides **6c**–**f** whereas diethyl 2-methylbenzylphosphonate (**6b**) yielded exclusively the *trans*-stilbene *trans*-**7b** (Scheme 2). Horner-Emmons olefination of the substituted benzaldehydes **9d**, **g**, furfural (**9h**) and pyridinecarbaldehyde (**9i**) gave the substituted *o*-bromo-*trans*-stilbenes **7d**, **g** and stilbene analogs **7h**, **i** with a furyl and pyridyl moiety, respectively. The olefination of benzaldehydes **11** and **9d** with substituted *o*-bromobenzyltriphenylphosphonium bromides **10j** and **10k** again gave mixtures of *cis*-**7j**, **k** and *trans*-**7j**, **k** with the *cis* isomer predominating (Scheme 2).

However, the *cis*-stilbenes *cis*-**7** could easily be photoisomerized[12] to the *trans*-isomers *trans*-**7** by irradiating solutions in CCl_4 in the presence of diphenyl disulfide (Scheme 3). Thus, a series of eight differently substituted *o*-bromo-*trans*-stilbenes *trans*-**7a**–**g**, **j**, **k** and two heterocyclic analogs *trans*-**7h**, **i** was at hand.

Scheme 2



6	X	R^1	*cis*-7 (%)	*trans*-7 (%)
a	PPh_3Cl	H	85	8
b	$P(O)(OEt)_2$	2-Me	0	92
c	PPh_3Br	4-Me	83	10
d	PPh_3Br	4-OMe	86	7
e	PPh_3Cl	3,5-(*t*Bu)$_2$	88	7
f	PPh_3Br	4-CO_2Me	87	8

9	Ar	*trans*-7 (%)
d	4-C_6H_4OMe	85
g	4-$C_6H_4NO_2$	70
h	2-furyl	82
i	2-pyridyl	80

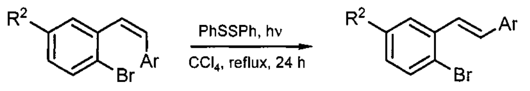
10	R^2		R^1
j	CO_2Et	11	H
k	CO_2Me	9d	OMe

cis-7	(%)	*trans*-7	(%)
j	66	j	11
k	78	k	5

When subjected to the conditions employed for the coupling of *o*-dibromobenzene (**1**) with styrene (**2**), authentic *trans*-**7a** gave an 80% yield of crystalline (*Z*)-**4a**, and all the substituted *o*-bromo-*trans*-stilbenes and analogs *trans*-**7b**–**k** except for the pyridine derivative *trans*-**7i** led to the correspondingly substituted 9,10-bis(arylmethylene)-9,10-dihydroanthracenes **4b**–**h**, **j**, **k** in good yields, too (Table 1). By comparison of the ^1H- and ^{13}C-NMR spectra of the whole series of compounds **4a**–**h**, **j**, **k** it was obvious that the unsubstituted **4a** as well as the substituted **4c**, **e** with alkyl substituents [4-Me and 3,5-(*t*Bu)$_2$, respectively] on the arylmethylene groups in a number of experiments were obtained as single (*Z*) diastereomers after column chromatography and crystallization (Scheme 4, Table 1, entries 1, 4, 7).

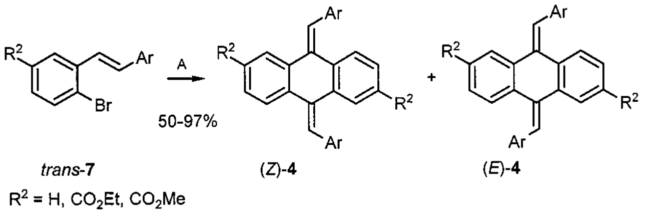
In two independent experiments carried out later with a different charge of reagents, however, mixtures of (*E*) and

Scheme 3



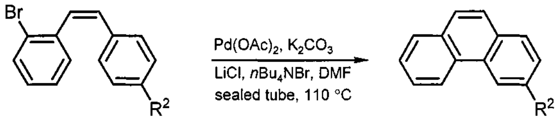
cis-**7**	R^2	Ar	*trans*-**7** (%)
a	H	C_6H_5	98
c	H	$4\text{-}C_6H_4Me$	98
d	H	$4\text{-}C_6H_4OMe$	93
e	H	$3,5\text{-}C_6H_3(tBu)_2$	90
f	H	$4\text{-}C_6H_4CO_2Me$	95
j	CO_2Et	C_6H_5	97
k	CO_2Me	$4\text{-}C_6H_4OMe$	94

Scheme 4. A: $Pd(OAc)_2$, K_2CO_3, LiCl, nBu_4NBr, DMF, 110°C, 20 h; for details see Table 1



(*Z*) diastereomers of **4a**, **c** were obtained (Table 1, entries 2, 5). On the other hand, **4d** with a strong donor group and **4f**, **g**, **j**, **k** with an acceptor group in either the arylmethylene moieties or the 9,10-dihydroanthracene skeleton were always isolated as mixtures of (*E*) and (*Z*) isomers with ratios varying from 1.8:1 to 1:2. The 9,10-bis(furylmethylene)-9,10-dihydroanthracene (**4h**) was also obtained as an (*E/Z*) mixture (1:1). There is no clear-cut rule as to when the (*E*) or the (*Z*) isomer predominates, and therefore it is not understood at this moment, why single isomers were isolated for **4a**, **c**, **e** in some cases and (*E/Z*) mixtures in others. But, apparently the (*Z*) diastereomers of **4a**, **4c**, and **4e** crystallize more rapidly, since the (*E*) -isomer could only be enriched in the mother liquors, yet never be isolated in pure crystalline form.

Scheme 5



cis-**7**	R^2	**12**	(%)
a	H	**a**	70
c	Me	**c**	71

The *o*-bromo-*cis*-stilbenes *cis*-**7a**, **c**, when subjected to the same conditions, did not yield any products of type **4**, but only phenanthrene (**12a**), and 3-methylphenanthrene (**12c**) in 70 and 71% yield, respectively, arising from an intramolecular aryl bromide to arene coupling (Scheme 5).

Mechanistic Considerations and Physical Properties of 9,10-Bis(arylmethylene)-9,10-dihydroanthracenes

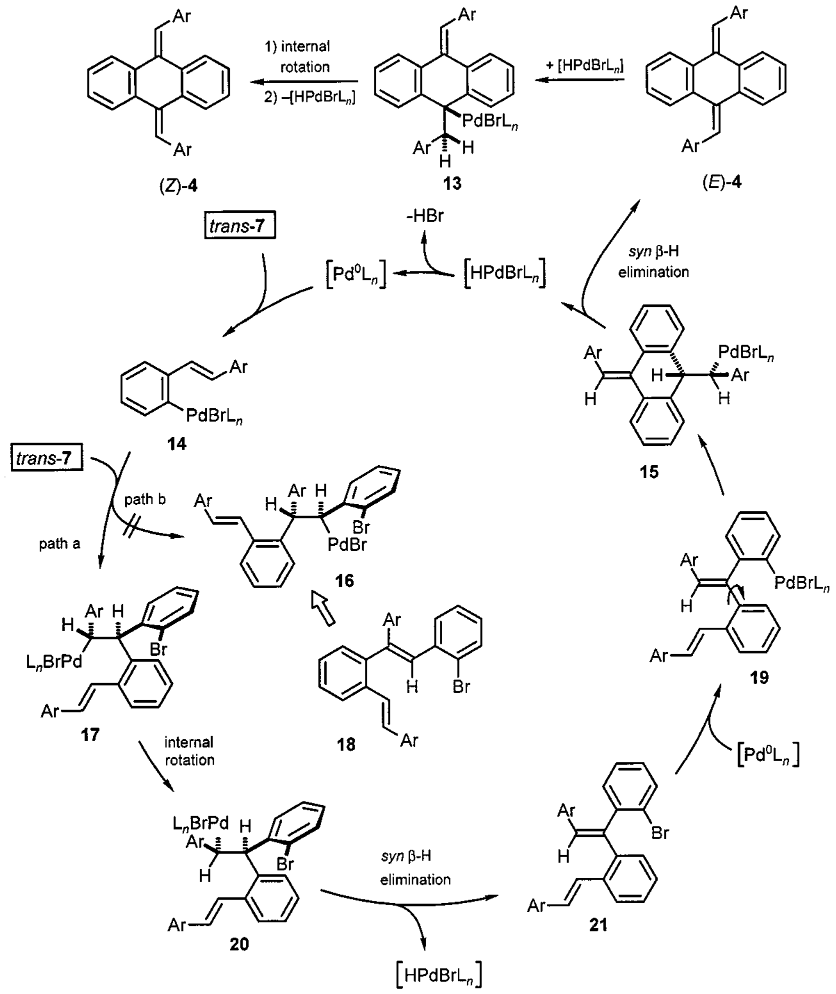
According to the generally accepted mechanism of the Heck reaction[1][2][3], the observed dehydrobrominative reaction of *o*-bromo-*trans*-stilbenes can be rationalized in terms of two sequences of oxidative addition, carbopalladation, and β-hydride elimination (Scheme 6). The first arylpalladium bromide intermediate **14** must add to the double bond of another molecule of *trans*-**7** regioselectively to give the σ-alkylpalladium intermediate **17** rather than **16**, as a β-hydride elimination product **18**, which would have been formed from **16**, or a consecutive product derived from **16** by 5-*exo*-*trig* ring closure[13], was never detected even in trace amounts. It is yet unknown, why the carbopalladation of *trans*-**7** by **14** occurs regioselectively, however, the reason cannot be a simple steric effect by the *o*-bromo substituent

Table 1. Pd-catalyzed self-cross coupling of *o*-bromo-*trans*-stilbenes and analogs **7** to give 9,10-bis(arylmethylene)-9,10-dihydroanthracenes **4** (see Scheme 4)

Entry	Starting material *trans*-**7**	R^2	Ar	Yield[a] (%)	Products	Ratio[b] (*E*)/(*Z*)
1	**a**	H	C_6H_5	80	(*Z*)-**4a**	0[c]
2	**a**	H	C_6H_5	88[d]	(*E/Z*)-**4a**	1:2.9[e]
3	**b**	H	$2\text{-}C_6H_4\text{-}Me$	88[d]	(*E/Z*)-**4b**	1:2.3
4	**c**	H	$4\text{-}C_6H_4\text{-}Me$	75	(*Z*)-**4c**	0[c]
5	**c**	H	$4\text{-}C_6H_4\text{-}Me$	97[d]	(*E/Z*)-**4c**	1:2.5[e]
6	**d**	H	$4\text{-}C_6H_4\text{-}OMe$	70	(*E/Z*)-**4d**	1:2
7	**e**	H	$3,5\text{-}C_6H_3\text{-}(tBu)_2$	50	(*Z*)-**4e**	0[c]
8	**f**	H	$4\text{-}C_6H_4\text{-}CO_2Me$	72	(*E/Z*)-**4f**	1:1
9	**g**	H	$4\text{-}C_6H_4\text{-}NO_2$	56	(*E/Z*)-**4g**	1.8:1
10	**h**	H	2-furyl	76	(*E/Z*)-**4h**	1:1
11	**i**	H	2-pyridyl	–[f]	–	–
12	**j**	CO_2Et	C_6H_5	78	(*E/Z*)-**4j**	1:1.1
13	**k**	CO_2Me	$4\text{-}C_6H_4\text{-}OMe$	64	(*E/Z*)-**4k**	2:3

[a] Isolated yields of pure products. – [b] Ratio refers to product mixture characterized by its ^1H NMR spectrum. – [c] In one series of experiments, only the (*Z*) diastereomer was isolated after subsequent purification by column chromatography and crystallization. – [d] Yield of crude isolated product. – [e] In an independent experiment, the (*E/Z*) ratio was determined for the crude product by ^1H-NMR spectroscopy. – [f] Only a mixture of products containing **4i** was obtained. The product **4i** decomposed upon attempted chromatographic purification.

Scheme 6. Suggested mechanism for the Pd-catalyzed reaction of *o*-bromo-*trans*-stilbenes

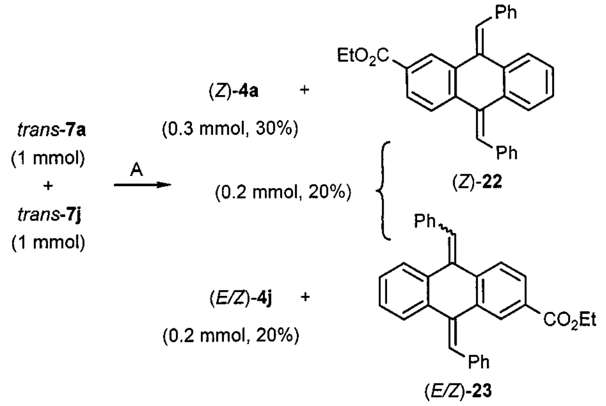


in one of the aryl groups, as the *o*-bromo-*o'*-methyl-*trans*-stilbene *trans*-**7b** also gave the corresponding dihydroanthracene derivative (*E/Z*)-**4b** in 88% yield[14]. The *syn*-β-hydride elimination from **17** after internal rotation to conformation **20** results in compound **21**, which can again oxidatively add to palladium(0). The resulting arylpalladium bromide intermediate **19** can undergo an intramolecular carbopalladation to give **15**. The usual *syn*-β-hydride elimination from **15** can only lead to (*E*)-**4**. Thus the (*Z*)-configurated products of type **4** must be formed by an unusual *anti*-β-hydride elimination or, more probably, by subsequent isomerization of (*E*)-**4**.

Such an isomerization can occur by readdition of [HPdBrL$_n$] to (*E*)-**4** in the reverse sense, internal rotation in the intermediate **13** and *syn*-elimination of [HPdBrL$_n$] involving the other β-hydride. (*E*)-to-(*Z*) isomerization of **4** could also be induced thermally. Indeed, a study of the temperature dependence of the ^{1}H-NMR spectra of compounds **4a**, **4d**, and **4g** disclosed that (*E*)-to-(*Z*) isomerization must be rapid, at least at elevated temperatures. While no short-term changes were detected in the spectrum of the unsubstituted compound (*Z*)-**4a** between 50 and 100 °C, a new set of signals became visible even after 5 min at 150 °C in [D$_6$]DMSO and reached a maximum intensity after 3.5 h. The complete set of signals could be extracted from the spectrum of the mixture, and there is no doubt that those signals were due to the (*E*) diastereomer (*E*)-**4a**. At the equilibrium at 150 °C the (*E/Z*) ratio had reached 0.8:1. Also according to the ^{1}H-NMR spectra, the (*E/Z*) ratio of the *p*-methoxy-substituted compound **4d** in [D$_6$]DMSO changed from 2.4:1 to 1.3:1 on going from 35 to 180 °C, and that of the *p*-nitro compound **4g** changed from 1.5:1 at 35 °C to 1:1.2 at 180 °C. These observations evidence that the barrier to rotation around the exocyclic double bonds of the 9,10-dihydroanthracene skeleton of compounds **4** must be lower than 20 kcal/mol. However, apparent differences in thermodynamic stabilities of diastereomers for differently substituted systems cannot be explained.

As has been observed for a number of other cross-coupling products,[3d][5] compounds **4** are formed in high yields only under the Jeffery conditions[6]. When the original Heck conditions [Pd(OAc)$_2$, PPh$_3$, NEt$_3$][15] were applied to *trans*-**7a**, the dehydrobromination product (*Z*)-**4a** was formed only in low yield (≤ 10%), and most of the starting material *trans*-**7a** was recovered. With Pd(PPh$_3$)$_4$ as a catalyst and NaOMe as a base in DMF, the reaction of *cis*-**7a**, **c**, **e**, **f** gave only the corresponding debromination products *cis*- and *trans*-stilbene, *cis*- and *trans*-4-methylstilbene, *cis*- and *trans*-3,5-di-*tert*-butylstilbenes, and *cis*- and *trans*-4-methoxycarbonylstilbenes, respectively. In a typical cross-over experiment, a 1:1 mixture of *trans*-**7a** and *trans*-**7j** was subjected to the optimized reaction conditions. This afforded a mixture of the "like" products (*Z*)-**4a** and (*E/Z*)-**4j** as well as the three cross-over products (*Z*)-**22**, (*Z*)-**23**, and (*E*)-**23**. The latter three could only be isolated as a mixture (20%), while (*Z*)-**4a** (30% yield) and (*E/Z*)-**4j** (20%) were isolated separately (Scheme 7). Finally, a mixture of *cis*-**7a** and *trans*-**7a** (1:1) was treated with the same catalyst. This gave phenanthrene (**12a**) in 71% yield based on the amount of *cis*-**7a** in the mixture and (*Z*)-**4a** based on the content of *trans*-**7a** with the same 80% as if pure *trans*-**7a** had reacted. This proved that *cis*-**7a** was not even incorporated into the intermediate arylpalladium intermediate **14**, although it was present in a considerable excess.

Scheme 7. A: Pd(OAc)$_2$, K$_2$CO$_3$, LiCl, nBu$_4$NBr, DMF, sealed tube, 110°C



Thus, a new palladium-catalyzed formation of six-membered rings has been established with the cyclizing self-cross coupling of *o*-bromo-*trans*-stilbenes and its analogs. This one-step procedure appears to be an efficient method for the regioselective synthesis of various 9,10-bis(arylmethylene)-9,10-dihydroanthracenes which, in same cases, crystallize as pure (*Z*) diastereomers.

The UV spectra of compounds **4a**, **c**−**k** are similar to that of anthracene, yet the ^1L_a band at the long-wavelength end, unlike that of anthracene, is broad and exhibits no vibrational structure probably due to the torsional mobility of the phenyl groups; as these "wings" are tilted with respect to the anthracene skeleton, substituents in the phenyl groups with the exception of **4g** cause only moderate bathochromic shifts. The strong electronic interaction of the nitro group in **4g** seems to stiffen the molecule leading to a somewhat larger shift and a vibrational structure of the longest wavelength band with a spacing of about 1400 cm^{-1}.

The electrochemical behaviour of (*Z*)-**4a** with an oxidation potential of +1.39 V (vs. Ag/AgCl) and a reduction potential of −1.75 V (vs. Ag/AgCl) is similar to that of anthracene. The values for anthracene, measured in the same solvent/conducting salt system, are +1.44 and −1.94 V (corr. to Ag/AgCl, measured against calomel[16]). The reduction of (*Z*)-**4a** becomes quasi-reversible at sufficiently high scan rates, whereas the oxidation remains irreversible up to a scan rate of 0.05 V/s. Most probably the radical cation of (*Z*)-**4a** like that of anthracene[17] is rapidly attacked by the solvent acetonitrile.

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Experimental Section

General: Melting points were determined with a Büchi 510 apparatus and are uncorrected. − NMR spectra were recorded with a Bruker AM 250, Varian Unity 300, or Varian Inova 500 spectrometer. ^{1}H-NMR (250 MHz, if not specified otherwise) chemical shifts are reported relative to CHCl$_3$ at $\delta = 7.26$ and tetramethylsilane at $\delta = 0.00$. Coupling constants are reported in Hz. In a few cases [compounds (*E/Z*)-**4j**, (*E/Z*)-**4k**, mixture of **22**/**23**] only relative intensities as fractions of protons have been given due to partial signal overlap. ^{13}C-NMR (62.9 MHz, if not specified otherwise) chemical shifts are expressed relative to CDCl$_3$ at $\delta = 77.00$ and tetramethylsilane at $\delta = 0.00$, multiplicities were determined by APT or DEPT. NMR-spectroscopic terms were reported by using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quadruplet; quint, quintuplet; m, multiplet; *, assignment is interchangeable. − Mass spectra (EIMS, HRMS) were obtained with Varian CH 7, MAT 731, and MAT 311 spectrometers and determined at an ionizing voltage of 70 eV; relevant data are tabulated as *m/z* values. − UV/Vis: Cary 219 (Varian). − Elemental analyses were performed at the Mikroanalytisches Laboratorium des Instituts für Organische Chemie der Georg-August-Universität Göttingen.

Unless otherwise stated, all reactions were carried out in oven-dried glassware. THF and Et$_2$O were distilled from sodium benzophenone ketyl. DMF and CH$_2$Cl$_2$ were distilled from CaH$_2$. CCl$_4$ was distilled from P$_2$O$_5$. Reagents were from commercial suppliers and used without further purification. All solutions were concentrated under reduced pressure with a rotary evaporator, and the residue was chromatographed on a silica gel column using petroleum ether/diethyl ether, petroleum ether/dichloromethane, or petroleum ether/ethyl acetate as the eluents unless specified otherwise. Flash chromatography was performed using E. Merck silica gel 60 (70−230 mesh). The plates used for thin-layer chromatography (TLC) were E. Merck silica gel 60 F$_{254}$ (0.25 mm thickness) precoated on aluminum plate, and they were visualized under both long (365 nm) and short (254 nm) UV light.

Designation of compounds **4** as (*E*) and (*Z*) isomers refers to the orientation of the phenyl groups (attached to the methylene carbon atoms in 9,10-position of the dihydroanthracene skeleton) relative to each other. The assignment is based on the observation that the ^{1}H-NMR signals of the methine protons of the (*Z*) isomer are shifted to higher field with respect to the (*E*) isomer as proven by the occurrence of accompanying AA′BB′ systems for protons 1,4-H and 2,3-H, respectively, of the dihydroanthracene skeleton. The (*E/Z*) ratio for compounds **4a**−**d**, **f**−**h**, **j**, **k** was determined mostly by integration of the methine and/or other suitable signals. Due to facile isomerization the ratio is influenced by the conditions during preparation and purification of the products.

(Z)-9,10-Bis(phenylmethylene)-9,10-dihydroanthracene [(*Z*)-**4a**]: A mixture of 1,2-dibromobenzene (1.0 g, 4.2 mmol), styrene (439 mg, 4.2 mmol), K_2CO_3 (1.4 g, 10 mmol), LiCl (178 mg, 4.2 mmol) and nBu_4NBr (1.4 g, 4.3 mmol) and $Pd(OAc)_2$ (45 mg, 0.2 mmol) in DMF (30 ml) was heated in a sealed tube at 110°C for 18 h. The resulting dark solution was poured into ice/water (200 ml), the mixture was extracted with diethyl ether (3 × 100 ml). The combined organic solution was washed with water (4 × 100 ml), dried ($MgSO_4$), and concentrated. Purification by column chromatography (SiO_2, 200 g, pentane/dichloromethane, 20:1) yielded *trans*-stilbene (22 mg, 3%), *trans*-1,2-distyrylbenzene (77 mg, 13%) and (*Z*)-**4a** (330 mg, 44%). (*Z*)-**4a**: Pale-yellow needles, m.p. 189−190°C. − UV (acetonitrile): λ_{max} (lg ε) = 221 nm (4.687), 245 (sh, 4.2), 332 (br., 4.324). − ^{1}H NMR (500 MHz, HH-COSY, $CDCl_3$): δ = 6.95 (AA′ part of an AA′BB′ system, 2 H, 1,4-H), 7.10 (s, 2 H, methine-H), 7.23 (tt, ^3J = 7.6, ^4J = 1.8 Hz, 2 H, 4′-H), 7.31 (t, ^3J = 7.6 Hz, 4 H, 3′,5′-H), 7.36 (2 BB′ parts of 2 AA′BB′ systems, 4 H, 2,3,6,7-H), 7.45 (dt, ^3J = 7.7, ^4J = 1.5 Hz, 4 H, 2′,6′-H), 7.81 (AA′ part of an AA′BB′ system, 2 H, 5,8-H). − ^{13}C NMR ($CDCl_3$): δ = 123.19, 126.38, 127.10, 128.59 (all d, C-1,2,3,4,5,6,7,8), 126.80 (d, methine-C), 127.27 (d, C-4′), 128.31 (d, C-3′), 129.44 (d, C-2′), 134.83, 135.80, 136.89, 137.58 (all s, C-1′,4a,8a,9a,10a,9,10). − MS (70 eV, EI); *m/z* (%): 356 (100) [M$^+$], 339 (14), 277 (8), 265 (24) [$M^+ - C_7H_7$], 176 (6), [$M^+ - C_{14}H_{12}$], 169 (12). − $C_{28}H_{20}$ (356.5): calcd. C 94.35, H 5.65; found C 94.28, H 5.66.

Crystal Structure Analysis of (Z)-9,10-Bis(phenylmethylene)-9,10-dihydroanthracene [(*Z*)-**4a**]: Single crystals suitable for X-ray crystallography were obtained by recrystallization from CH_2Cl_2/EtOH (10:1). $C_{28}H_{20}$, *M* = 356, orthorhombic, space group $Pca2_1$, *a* = 21.932(4), *b* = 12.192(2), *c* = 7.132(1) Å, *V* = 1907.1(10) Å^3, *Z* = 4; *R* = 0.052, R_w = 0.052. Data for a crystal of dimensions 0.3 × 0.6 × 0.1 mm were measured with a Nicolet R3m/v diffractometer (7.0° < 2θ < 45°) with Mo-K_α radiation using ω scans. 1363 independent reflections were measured and of these 1126 had [$F_o > 3.0\,\sigma(F_o)$] and were considered to be observed. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were included in field-calculated positions with assigned isotropic temperature factors. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101355. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

General Procedure for the Preparation of 2-Bromo-cis- and -trans-stilbenes

2-Bromo-cis- and -trans-stilbene (*cis- and trans-***7a**)

(i) Wittig Olefination of 2-Bromobenzaldehyde: To a stirred solution of benzyltriphenylphosphonium chloride (**6a**) (3.9 g, 10 mmol) in THF (40 ml) under argon at 0°C was added dropwise a 2.5 M solution of *n*BuLi in hexane (4 ml, 10 mmol). The red solution was stirred for 30 min. A solution of 2-bromobenzaldehyde (1.9 g, 10 mmol) in THF (5 ml) was added dropwise, discoloring the solution. The reaction solution was then warmed to room temperature, and then further stirred for 0.5 h. After addition of water (100 ml), the mixture was extracted with petroleum ether (3 × 100 ml). The combined organic extracts were dried with $MgSO_4$ and concentrated. Purification by chromatography on silica gel (100 g, petroleum ether) yielded 2-bromo-*cis*-stilbene (*cis*-**7a**) (2.2 g, 85%) and *trans* isomer (*trans*-**7a**) (210 mg, 8%). *cis*-**7a**: Colorless oil. − ^{1}H NMR ($CDCl_3$): δ = 6.64 (d, ^3J = 12.1 Hz, 1 H, *cis*-olefin-H), 6.72 (d, ^3J = 12.1 Hz, 1 H, *cis*-olefin-H), 7.11 (m, 2 H), 7.15−7.23 (m, 6 H), 7.63 (m, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 123.86 (s), 126.91 (d), 127.25 (d), 128.09 (d), 128.59 (d), 128.91 (d), 129.39 (d), 130.77 (d), 131.32 (d), 132.60 (d), 136.23 (s), 137.87 (s).

(ii) Photo-Induced Isomerization of 2-Bromo-cis-stilbene (*cis*-**7a**): A mixture of 2-bromo-*cis*-stilbene (*cis*-**7a**) (518 mg, 2.0 mmol) and diphenyl disulfide (218 mg, 1.0 mmol) in CCl_4 (20 ml) was irradiated with a daylight lamp (500 W) under reflux for 24 h. Concentration and column chromatography on silica gel gave 2-bromo-*trans*-stilbene (*trans*-**7a**) (507 mg, 98%) as a colorless oil. − ^{1}H NMR ($CDCl_3$): δ = 7.06 (d, ^3J = 16.2 Hz, 1 H, *trans*-olefin-H), 7.13 (dt, ^3J = 7.6, ^4J = 1.7 Hz, 1 H), 7.30−7.44 (m, 4 H), 7.50 (d, ^3J = 16.2 Hz, 1 H, *trans*-olefin-H), 7.58 (d, ^3J = 6.9 Hz, 2 H), 7.59 (dd, ^3J = 7.8, ^4J = 1.6 Hz, 1 H), 7.67 (dd, ^3J = 7.8, ^4J = 1.6 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 124.09 (s), 126.63 (d), 126.77 (d), 127.34 (d), 127.47 (d), 127.99 (d), 128.66 (d), 131.37 (d), 132.98 (d), 136.92 (s), 137.03 (s). − MS (70 eV, EI); *m/z* (%): 260/258 (56/54) [M$^+$], 179 (100) [$M^+ - Br$], 178 (96), 152 (45), 102 (18) [$M^+ - Br - C_6H_5$], 89 (86), 76 (74). − $C_{14}H_{11}Br$ (259.1): calcd. C 64.89, H 4.28; found C 64.87, H 4.27.

Diethyl 2-Methylbenzylphosphonate (**6b**): A mixture of 2-methylbenzyl chloride (14.06 g, 100 mmol) and triethyl phosphite (17.78 g, 107 mmol) was stirred under N_2 at 160°C for 17 h. Distillation gave **6b** (23.36 g, 96%) as a colorless liquid, b.p. 127°C/0.005 Torr. − ^{1}H NMR ($CDCl_3$, CH_2Cl_2 as internal standard): δ = 1.24 (t, ^3J = 7.0 Hz, 6 H, CH_3), 2.39 (s, 3 H, CH_3), 3.18 (d, $^2J_{PH}$ = 21.9 Hz, 2 H, PCH_2), 4.00 (qui, ^3J = 7.0, $^3J_{PH}$ = 7.0 Hz, 4 H, OCH_2), 7.10−7.20 (m, 3 H, phenyl-H), 7.20−7.30 (m, 1 H, phenyl-H). − ^{13}C NMR ($CDCl_3$): δ = 16.11 (d, $^3J_{PC}$ = 6 Hz, CH_2CH_3), 19.71 (CH_3), 30.77 (d, $^1J_{PC}$ = 138 Hz, PCH_2), 61.78 (d, $^2J_{PC}$ = 7 Hz, OCH_2), 125.73 (d, $^4J_{PC}$ = 4 Hz, CH), 126.78 (d, $^4J_{PC}$ = 4 Hz, CH), 129.77 (d, $^2J_{PC}$ = 9 Hz, C-1), 130.17 (d, $^5J_{PC}$ = 3 Hz, C-4), 130.32 (d, $^3J_{PC}$ = 6 Hz, C-6), 136.71 (d, $^3J_{PC}$ = 7 Hz, C-2).

2-Bromo-2′-methyl-trans-stilbene (*trans*-**7b**): To a suspension of NaH [1.20 g, 30.0 mmol, 60% in mineral oil, washed with pentane (3 × 10 ml) under N_2] in dry THF (50 ml) was added at 0°C phosphonate **6b** (7.49 g, 30.9 mmol) with stirring. After warming up the mixture to room temperature and refluxing for a few minutes, 2-bromobenzaldehyde (5.00 g, 27.0 mmol) was added at 0°C via a cannula and the mixture stirred at room temperature for 18 h. The mixture was diluted with diethyl ether (400 ml), washed with water (4 × 100 ml), the organic phase dried ($MgSO_4$) and concentrated. Column chromatography (SiO_2, 25 g, pentane, R_f = 0.4) yielded *trans*-**7b** (6.789 g, 92%) as a colorless solid, m.p. 49°C. − ^{1}H NMR (500 MHz, HH-COSY, $CDCl_3$): δ = 2.43 (s, 3 H, CH_3), 7.11 (td, *J* = 7.7, 1.7 Hz, 1 H, 5-H), 7.16−7.25 (m, 3 H), 7.24 and 7.33 (AB system, J_{AB} = 16.1 Hz, 2 H, *trans*-olefin-H), 7.31 (bt, *J* = 7.9 Hz, 1 H, 4-H), 7.58 (dd, *J* = 8.0, 1.2 Hz, 1 H, 6-H), 7.63 (dd, *J* = 8.0, 1.7 Hz, 1 H, 6′-H), 7.66 (dd, *J* = 7.9, 1.6 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 19.95 (q, CH_3), 124.10 (s, CBr), 125.79 (d, C-5), 126.27 (d), 126.85 (d), 127.52 (d), 127.94 (d), 128.74 (d, 2 C, methine-C), 129.28 (d), 130.43 (d), 133.02 (d), 135.95 (s, C-2′*), 136.01 (s, C-1′*), 137.45 (s, C-1). − $C_{15}H_{13}Br$ (273.2): calcd. C 65.95, H 4.80, Br 29.25; found C 66.17, H 5.03, Br 29.01.

2-Bromo-4′-methyl-cis-stilbene (*cis*-**7c**): Compound *cis*-**7c** was obtained as a colorless oil (2.3 g, 83%), contaminated with up to 10% of *trans*-**7c** according to its ^{1}H-NMR spectrum, by Wittig olefination of 2-bromobenzaldehyde (**5**) (1.9 g, 10 mmol) with (4-

methylbenzyl)triphenylphosphonium bromide (**6c**) (4.47 g, 10 mmol). − ^{1}H NMR ($CDCl_3$): δ = 2.31 (s, 3 H, Me), 6.60 and 6.68 (AB system, J_{AB} = 12.1 Hz, 2 H, *cis*-olefin-H), 7.00−7.13 (m, 6 H), 7.23−7.26 (m, 1 H), 7.61−7.65 (m, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 21.17 (q), 123.88 (s), 126.94 (d), 128.51 (d), 128.62 (d), 128.84 (d), 128.88 (d), 130.80 (d), 131.27 (d), 132.62 (d), 133.37 (s), 137.08 (s), 138.16 (s).

2-Bromo-4′-methyl-trans-stilbene (*trans*-**7c**): Compound *trans*-**7c** was obtained as a colorless oil (2.6 g, 98%) by photo-induced isomerization of 2-bromo-4′-methyl-*cis*-stilbene (*cis*-**7c**) (2.7 g, 10 mmol). − ^{1}H NMR ($CDCl_3$): δ = 2.46 (s, 3 H, Me), 7.09 (d, ^{3}J = 16.2 Hz, 1 H, *trans*-olefin-H), 7.16 (dt, ^{3}J = 8.1, ^{4}J = 1.7 Hz, 1 H), 7.26 (d, ^{3}J = 8.0 Hz, 2 H), 7.36 (dt, ^{3}J = 8.1, ^{4}J = 1.7 Hz, 1 H), 7.53 (d, ^{3}J = 16.1 Hz, 1 H, *trans*-olefin-H), 7.54 (d, ^{3}J = 8.0 Hz, 2 H), 7.66 (dd, ^{3}J = 7.9, ^{4}J = 0.7 Hz, 1 H), 7.72 (dd, ^{3}J = 7.9, ^{4}J = 0.7 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 21.23 (q), 124.00 (s), 126.32 (d), 126.51 (d), 126.70 (d), 127.42 (d), 128.47 (d), 129.37 (d), 131.30 (d), 132.95 (d), 134.18 (s), 137.20 (s), 137.90 (s). − MS (70 eV, EI), *m/z* (%): 274/272 (73/70) [M$^+$], 193 (33) [M$^+$ − Br], 178 (100) [M$^+$ − Br − Me]. − $C_{15}H_{13}Br$ (273.2): calcd. C 65.95, H 4.80; found C 65.87, H 4.80.

2-Bromo-4′-methoxy-cis- and -trans-stilbene (*cis*- and *trans*-**7d**): Compound *cis*- and *trans*-**7d** were obtained in 93% yield (2.7 g, ratio 12:1) as a mixture by Wittig olefination of 2-bromobenzaldehyde (**5**) (1.9 g, 10 mmol) with 4-methoxybenzyltriphenylphosphonium bromide (**6d**) (4.6 g, 10 mmol). Photo-induced isomerization of the mixture (2.7 g) gave *trans*-**7d** (2.7 g, 93%) as colorless crystals. 2-Bromo-4′-methoxy-*trans*-stilbene (*trans*-**7d**) (2.5 g, 85%) was also prepared by Horner-Emmons olefination of 4-methoxybenzaldehyde (**9d**) (1.4 g, 10 mmol) and diethyl 2-bromobenzylphosphonate (**8**) (3.1 g, 10 mmol) as colorless crystals. M.p. 64−65°C. − ^{1}H NMR ($CDCl_3$): δ = 3.85 (s, 3 H, OMe), 6.94 (dd, ^{3}J = 8.7, ^{4}J = 1.8 Hz, 2 H), 6.96 (d, ^{3}J = 16.2 Hz, 1 H, *trans*-olefin-H), 7.11 (dt, ^{3}J = 7.9, ^{4}J = 1.6 Hz, 1 H), 7.31 (dt, ^{3}J = 7.9, ^{4}J = 1.6 Hz, 1 H), 7.37 (d, ^{3}J = 16.2 Hz, 1 H, *trans*-olefin-H), 7.52 (dd, ^{3}J = 8.7, ^{4}J = 1.8 Hz, 2 H), 7.60 (dd, ^{3}J = 7.9, ^{4}J = 1.3 Hz, 1 H), 7.67 (dd, ^{3}J = 7.9, ^{4}J = 1.3 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 55.20 (q), 114.13 (d), 123.87 (s), 125.21 (d), 126.39 (d), 127.42 (d), 128.03 (d), 128.28 (d), 129.79 (s), 130.92 (d), 132.94 (d), 137.34 (s), 159.62 (s). − MS (70 eV, EI); *m/z* (%): 290/288 (98/100) [M$^+$], 194 (38) [M$^+$ − Br − Me], 166 (60) [M$^+$ − Br − COMe], 165 (90) [M$^+$ − HBr − COMe]. − $C_{15}H_{13}BrO$ (289.2): calcd. C 62.30, H 4.53; found C 62.35, H 4.43.

2-Bromo-3′,5′-di-tert-butyl-cis-stilbene (*cis*-**7e**): Compound *cis*-**7e** was obtained as a colorless oil (3.3 g, 88%) by Wittig olefination of 2-bromobenzaldehyde (**5**) (1.9 g, 10 mmol) with (3,5-di-*tert*-butylbenzyl)triphenylphosphonium chloride (**6e**) (5.0 g, 10 mmol). − ^{1}H NMR ($CDCl_3$): δ = 1.18 (s, 18 H, 6 × Me), 6.58 (d, ^{3}J = 12.1 Hz, 1 H, *cis*-olefin-H), 6.69 (d, ^{3}J = 12.1 Hz, 1 H), 6.99 (d, ^{4}J = 1.5 Hz, 2 H), 7.08−7.13 (m, 2 H), 7.21−7.26 (m, 2 H), 7.61−7.65 (m, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 31.30 (q), 34.59 (s), 121.29 (d), 123.57 (d), 123.85 (s), 126.99 (d), 128.42 (d), 128.68 (d), 130.91 (d), 132.38 (d), 132.61 (d), 135.22 (s), 138.74 (s), 150.32 (s).

2-Bromo-3′,5′-di-tert-butyl-trans-stilbene (*trans*-**7e**): Compound *trans*-**7e** was obtained as a colorless oil (1.7 g, 90%) by photo-induced isomerization of 2-bromo-3′,5′-di-*tert*-butyl-*cis*-stilbene (*cis*-**7e**) (1.9 g, 5.1 mmol). − ^{1}H NMR ($CDCl_3$): δ = 1.44 (s, 18 H, 6 × Me), 7.15 (t, ^{3}J = 7.4 Hz, 1 H), 7.16 (d, ^{3}J = 16.1 Hz, 1 H, *trans*-olefin-H), 7.36 (t, ^{3}J = 7.4 Hz, 1 H), 7.47 (s, 3 H), 7.52 (d, ^{3}J = 16.1 Hz, 1 H, *trans*-olefin-H), 7.64 (dd, ^{3}J = 8.0, ^{4}J = 1.2 Hz, 1 H), 7.73 (dd, ^{3}J = 8.0, ^{4}J = 1.2 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 31.45 (q), 34.84 (s), 121.15 (d), 122.52 (d), 124.04 (s), 126.73 (d), 126.90 (d), 127.48 (d), 128.53 (d), 132.63 (d), 132.99 (d), 136.27 (s), 137.49 (s), 151.11 (s). − MS (70 eV, EI); *m/z* (%): 372/370 (51/50) [M$^+$], 357/355 (43/42) [M$^+$ − Me], 276 (4) [M$^+$ − Br − Me], 204 (15) [M$^+$ − Br − *t*Bu − 2 × Me], 189 (100) [M$^+$ − Br − *t*Bu − 3 × Me]. − $C_{22}H_{27}Br$ (371.4): calcd. C 71.16, H 7.33; found C 71.13, H 7.32.

2-Bromo-4′-methoxycarbonyl-cis-stilbene (*cis*-**7f**): Compound *cis*-**7f** was obtained as colorless crystals (2.7 g, 87%) by Wittig olefination of 2-bromobenzaldehyde (**5**) (1.9 g, 10 mmol) with (4-methoxycarbonylbenzyl)triphenylphosphonium bromide (**6f**) (4.9 g, 10 mmol). M.p. 58−59°C. − ^{1}H NMR ($CDCl_3$): δ = 3.88 (s, 3 H, OMe), 6.72 (s, 2 H), 7.09−7.11 (m, 3 H), 7.19 (d, ^{3}J = 8.2 Hz, 2 H), 7.60−7.63 (m, 1 H), 7.85 (d, ^{3}J = 8.2 Hz, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 51.93 (q), 123.78 (s), 127.09 (d), 128.81 (d), 128.87 (d), 129.61 (d), 129.44 (d), 130.43 (d), 130.72 (d), 131.59 (d), 132.79 (d), 137.42 (s), 141.08 (s), 166.71 (C=O).

2-Bromo-4′-methoxycarbonyl-trans-stilbene (*trans*-**7f**): Compound *trans*-**7f** was obtained as a colorless oil (1.5 g, 95%) by photo-induced isomerization of 2-bromo-4′-methoxycarbonyl-*cis*-stilbene (*cis*-**7f**) (1.6 g, 5.0 mmol). M.p. 81−82°C. − ^{1}H NMR ($CDCl_3$): δ = 3.90 (s, 3 H, OMe), 7.00 (d, ^{3}J = 16.2 Hz, 1 H, *trans*-olefin-H), 7.10 (dt, ^{3}J = 7.9, ^{4}J = 1.6 Hz, 1 H), 7.27 (dt, ^{3}J = 7.5 Hz, ^{4}J = 1.5 Hz, 1 H), 7.51−7.63 (m, 5 H), 8.01 (dd, ^{3}J = 8.4, ^{4}J = 1.9 Hz, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 51.87 (q), 124.24 (s), 126.45 (d), 126.63 (d), 127.43 (d), 129.13 (d), 129.56 (d), 129.84 (d), 130.03 (d), 132.96 (d), 136.32 (s), 141.16 (s), 166.51 (C=O). − MS (70 eV, EI); *m/z* (%): 318/316 (61/60) [M$^+$], 287/285 (22/22) [M$^+$ − OMe], 206 (9) [M$^+$ − Br − OMe], 178 (100) [M$^+$ − Br − CO_2Me]. − $C_{16}H_{13}BrO_2$ (317.2): calcd. C 60.59, H 4.13; found C 60.78, H 4.18.

2-Bromo-4′-nitro-trans-stilbene (*trans*-**7g**): Compound *trans*-**7g** was prepared by Horner-Emmons olefination of 4-nitrobenzaldehyde (**9g**) (1.5 g, 10 mmol) with diethyl 2-bromobenzylphosphonate (3.1 g, 10 mmol) to give *trans*-**7g** (2.1 g, 70%) as red crystals. M.p. 140−141°C. − ^{1}H NMR ($CDCl_3$): δ = 7.07 (d, ^{3}J = 16.2 Hz, 1 H), 7.18 (dt, ^{3}J = 7.8, ^{4}J = 1.7 Hz, 1 H), 7.35 (dt, ^{3}J = 7.8, ^{4}J = 1.0 Hz, 1 H), 7.60−7.70 (m, 5 H), 8.23 (d, ^{3}J = 8.8 Hz, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 124.02 (d), 124.54 (s), 126.82 (d), 127.12 (d), 127.66 (d), 128.80 (d), 129.82 (d), 131.70 (d), 133.18 (d), 135.86 (s), 142.35 (s), 146.89 (s). − MS (70 eV, EI); *m/z* (%): 305/303 (42/41) [M$^+$], 259/257 (2/2) [M$^+$ − NO_2], 224 (1) [M$^+$ − Br], 178 (100) [M$^+$ − Br − NO_2]. − $C_{14}H_{10}BrNO_2$ (304.1): calcd. C 55.29, H 3.31, N 4.61; found C 55.32, H 3.41, N 4.59.

1-Bromo-2-(trans-2-furylvinyl)benzene (*trans*-**7h**): Compound *trans*-**7h** was prepared by Horner-Emmons olefination of 2-furaldehyde (**9h**) (1.0 g, 10 mmol) with diethyl 2-bromobenzylphosphonate (**8**) (3.1 g, 10 mmol) to give *trans*-**7h** (2.0 g, 82%) as a colorless oil. − ^{1}H NMR ($CDCl_3$): δ = 6.42−6.46 (m, 2 H), 6.86 (d, ^{3}J = 16.0 Hz, 1 H, *trans*-olefin-H), 7.10 (dt, ^{3}J = 8.0, ^{4}J = 0.6 Hz, 1 H), 7.29 (t, ^{3}J = 8.0 Hz, 1 H), 7.40 (d, ^{3}J = 16.0 Hz, 1 H, *trans*-olefin-H), 7.45 (s, 1 H), 7.57−7.62 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 109.52 (d), 116.64 (d), 118.82 (d), 123.92 (s), 125.37 (d), 126.05 (d), 127.38 (d), 128.56 (d), 133.00 (d), 136.56 (s), 142.46 (d), 152.77 (s). − MS (70 eV, EI); *m/z* (%): 250/248 (98/100) [M$^+$], 169 (8) [M$^+$ − Br]. − $C_{12}H_9BrO$ (249.1): calcd. C 57.86, H 3.64; found C 57.78, H 3.63.

1-Bromo-2-(trans-2′-pyridylvinyl)benzene (*trans*-**7i**): Compound *trans*-**7i** was prepared by Horner-Emmons olefination of pyridine-2-carbaldehyde (**9i**) (1.1 g, 10 mmol) with diethyl 2-bromobenzylphosphonate (**8**) (3.1 g, 10 mmol) to give *trans*-**7i** (2.1 g, 80%) as a colorless oil. − ^{1}H NMR ($CDCl_3$): δ = 7.09−7.17 (m, 3 H), 7.30 (dt, ^{3}J = 7.9, ^{4}J = 0.6 Hz, 1 H), 7.45 (d, ^{3}J = 8.0 Hz, 1 H), 7.57−7.72 (m, 3 H), 7.94 (d, ^{3}J = 16 Hz, 1 H), 8.61 (d, ^{3}J = 4.1

Hz, 1 H). − ^{13}C NMR (CDCl$_3$): δ = 121.79 (d), 122.15 (d), 124.38 (s), 126.83 (d), 127.36 (d), 129.19 (d), 130.78 (d), 131.02 (d), 132.90 (d), 136.24 (d), 136.28 (s), 149.52 (d), 155.02 (s). − MS (70 eV, EI); *m/z* (%): 261/259 (9/9) [M$^+$], 180 (100) [M$^+$ − Br]. − $C_{13}H_{10}BrN$ (260.1): calcd. C 60.02, H 3.87, N 5.38; found C 60.10, H 3.84, N 5.29.

2-Bromo-5-ethoxycarbonyl-cis-stilbene (*cis*-**7j**) *and 2-Bromo-5-ethoxycarbonyl-trans-stilbene* (*trans*-**7j**): Compounds *cis*- and *trans*-**7j** were obtained in 77% yield (2.5 g, ratio 6:1) as a mixture by Wittig olefination of benzaldehyde (**11**) (1.1 g, 10 mmol) with (2-bromo-5-ethoxycarbonylbenzyl)triphenylphosphonium bromide (**10j**) (5.8 g, 10 mmol). Photoinduced isomerization of the mixture (2.5 g) gave *trans*-**7j** (2.4 g, 97%) as colorless crystals. M.p. 59−60°C. − ^{1}H NMR (CDCl$_3$): δ = 1.43 (t, ^3J = 7.2 Hz, 3 H, Me), 4.31 (q, ^3J = 7.1 Hz, 2 H, CH$_2$), 7.14 (d, ^3J = 16.2 Hz, 1 H, *trans*-olefin-H), 7.31−7.43 (m, 4 H), 7.56−7.65 (m, 3 H), 7.55 (dd, ^3J = 8.3, ^4J = 2.1 Hz, 1 H), 8.32 (d, ^4J = 2.0 Hz, 1 H). − ^{13}C NMR (CDCl$_3$): δ = 14.17 (q), 61.13 (t), 126.20 (d), 126.78 (d), 127.48 (d), 128.10 (d), 128.63 (d), 128.79 (s), 128.95 (d), 129.78 (s), 132.41 (d), 132.99 (d), 136.48 (s), 137.20 (s), 165.69 (C=O). − MS (70 eV, EI); *m/z* (%): 332/330 (58/60) [M$^+$], 287/285 (10/17) [M$^+$ − OEt], 252 (10), 206 (11) [M$^+$ − Br − OEt], 178 (100) [M$^+$ − Br − CO$_2$Et]. − $C_{17}H_{15}BrO_2$ (331.2): calcd. C 61.65, H 4.56; found C 61.60, H 4.39.

2-Bromo-5-methoxycarbonyl-4′-methoxy-cis-stilbene (*cis*-**7k**): Compound *cis*-**7k** was prepared as colorless crystals (2.7 g, 78%), contaminated with up to 5% of *trans*-**7k** according to its ^{1}H-NMR spectrum, by Wittig olefination of 4-methoxybenzaldehyde (**9d**) (1.4 g, 10 mmol) with (2-bromo-5-methoxycarbonylbenzyl)triphenylphosphonium bromide (**10k**) (5.7 g, 10 mmol). M.p. 70−71°C. − ^{1}H NMR (CDCl$_3$): δ = 3.74 (s, 3 H, OMe), 3.81 (s, 3 H, CO$_2$Me), 6.46 (d, ^3J = 12.0 Hz, 1 H, *cis*-olefin-H), 6.66 (d, ^3J = 12.0 Hz, 1 H, *cis*-olefin-H), 6.70 (d, ^3J = 8.6 Hz, 2 H), 7.04 (d, ^3J = 8.6 Hz, 2 H), 7.65−7.77 (m, 2 H), 7.89 (d, ^4J = 1.8 Hz, 1 H). − ^{13}C NMR (CDCl$_3$): δ = 52.09 (q), 55.06 (q), 113.63 (d), 126.39 (d), 128.33 (s), 129.12 (d), 129.19 (s), 129.22 (s), 130.13 (d), 131.70 (d), 131.79 (d), 132.87 (d), 138.83 (s), 158.96 (s), 166.15 (C=O).

2-Bromo-5-methoxycarbonyl-4′-methoxy-trans-stilbene (*trans*-**7k**): Compound *trans*-**7k** was obtained as colorless crystals (1.6 g, 94%) by photo-induced isomerization of 2-bromo-5-methoxycarbonyl-4′-methoxy-*trans*-stilbene (*cis*-**7k**) (1.7 g, 4.9 mmol). M.p. 130−131°C. − ^{1}H NMR (CDCl$_3$): δ = 3.80 (s, 3 H, OMe), 3.90 (s, 3 H, CO$_2$Me), 6.88 (d, ^3J = 8.7 Hz, 2 H), 7.06 (d, ^3J = 16.2 Hz, 1 H, *trans*-olefin-H), 7.26 (d, ^3J = 16.2 Hz, 1 H, *trans*-olefin-H), 7.47 (d, ^3J = 8.7 Hz, 2 H), 7.57−7.70 (m, 2 H), 8.26 (d, ^4J = 2.0 Hz, 1 H). − ^{13}C NMR (CDCl$_3$): δ = 52.28 (q), 55.29 (q), 114.18 (d), 124.12 (d), 127.40 (d), 128.24 (d), 128.69 (d), 128.83 (s), 129.44 (s), 129.52 (s), 132.14 (d), 133.18 (d), 137.70 (s), 159.85 (s), 166.44 (C=O). − MS (70 eV, EI); *m/z* (%): 348/346 (100/98) [M$^+$], 315 (4) [M$^+$ − OMe], 266 (8) [M$^+$ − HBr], 208 (15) [M$^+$ − Br − CO$_2$Me]. − $C_{17}H_{15}BrO_3$ (347.2): calcd. C 58.81, H 4.35; found C 58.79, H 4.51.

General Procedure for the Palladium-Catalyzed Reaction of 2-Bromo-trans-stilbenes to (Z or/and E)-9,10-Bis(arylmethylene)-9,10-dihydroanthracenes

(Z)-9,10-Bis(phenylmethylene)-9,10-dihydroanthracene [(*Z*)-**4a**]: A mixture of 2-bromo-*trans*-stilbene (*trans*-**7a**) (518 g, 2.0 mmol), K$_2$CO$_3$ (1.4 g, 10 mmol), LiCl (127 mg, 3.0 mmol), *n*Bu$_4$NBr (644 mg, 2.0 mmol), and Pd(OAc)$_2$ (45 mg, 0.2 mmol) in DMF (20 ml) was heated in a sealed tube at 110°C for 20 h. After addition of ice/water (200 ml) and cooling to room temperature, the mixture was extracted with ether (3 × 100 ml). The combined organic solutions were washed with water (4 × 100 ml), dried (MgSO$_4$), and concentrated. Purification by column chromatography (SiO$_2$, 200 g, pentane/dichloromethane, 20:1) yielded (*Z*)-**4a** (285 mg, 80%) as pale-yellow needles. The physical and spectroscopic data are identical with those of an authentic sample prepared from *o*-dibromobenzene and styrene (see above).

(E/Z)-9,10-Bis(phenylmethylene)-9,10-dihydroanthracene [(*E/Z*)-**4a**]: From a reaction of 2-bromo-*trans*-stilbene (*trans*-**7a**) (2.072 g, 8.0 mmol) with K$_2$CO$_3$ (5.528 g, 40.0 mmol), LiCl (508 mg, 12.0 mmol), *n*Bu$_4$NBr (2.579 g, 8.0 mmol), and Pd(OAc)$_2$ (180 mg, 0.8 mmol), carried out as above, was obtained 1.25 g (88%) of crude product after filtration through 60 g of flash silica gel eluting with pentane/CH$_2$Cl$_2$ (10:1). According to its ^{1}H- and ^{13}C-NMR spectra it was a 1:2.9 mixture of (*E*) and (*Z*) isomers. Crystallization from hexane gave 762 mg (53%) of pure (*Z*)-**4a**, and 480 mg of a 2:1 mixture of (*E*)-**4a** and (*Z*)-**4a**. − (*E*)-**4a**: ^{1}H NMR (500 MHz, HH-COSY, CDCl$_3$): δ = 7.01 (dt, A part of an ABCD system, *J* = 7.8, *J* = 1.2 Hz, 2 H, 2,6-H), 7.16 (s, 2 H, methine-H), 7.20−7.30 and 7.35−7.38 (m, overlapping signals of (*E*)- and (*Z*)-**4a**, phenyl-H), 7.27 (m, B part of an ABCD system, 3,7-H), 7.40 (dt, *J* = 8.2, *J* = 0.8 Hz, 4 H, phenyl-H), 7.54 (m, C part of an ABCD system, 2 H, 1,5-H), 7.79 (dd, D part of an ABCD system, *J* = 7.9, *J* = 0.9 Hz, 2 H, 4,8-H), due to signal overlap of (*E*)- and (*Z*)-**4a** some integrals could not be determined. − ^{13}C NMR (CDCl$_3$): δ = 123.71, 125.82, 127.61, 131.17 (all d, C-1,2,3,4,5,6,7,8), 126.62 (d, methine-C), 127.05 (d, C-4′), 128.20 (d, C-3′), 129.30 (d, C-2′), 132.33, 135.61, 137.38, 139.08 (all s, C-1′,4a,8a,9a,10a,9,10).

(E/Z)-9,10-Bis(2′-methylphenylmethylene)-9,10-dihydroanthracene [(*E/Z*)-**4b**]: A mixture of 2-bromo-2′-methyl-*trans*-stilbene (*trans*-**7b**) (1.092 g, 4.00 mmol), K$_2$CO$_3$ (2.800 g, 20.3 mmol), LiCl (0.254 g, 6.0 mmol), *n*Bu$_4$NBr (1.288 g, 4.0 mmol), and dry DMF (40 ml) in a Pyrex bottle was purged with N$_2$ for 10 min. Pd(OAc)$_2$ (90 mg, 0.40 mmol) was added and the sealed bottle heated at 110°C for 20 h with stirring. Workup as described above and flash chromatography [SiO$_2$, 30 g, pentane/dichloromethane (9:1), R_f = 0.45] gave (*E/Z*)-**4b** (674 mg, 88%) as a yellow solid (*E/Z* = 1:2.3 according to ^{1}H NMR). The (*Z*) isomer could only be enriched (451 mg, *E/Z* = 1:2.8, *E/Z* in the mother liquor = 1:1) by recrystallization from *n*-heptane (10 ml). − (*E/Z*)-**4b**: ^{1}H NMR (300 MHz, 500 MHz HH-COSY, CDCl$_3$): δ = 2.38 [s, 6 H, CH$_3$, (*E*)], 2.40 [s, 6 H, CH$_3$, (*Z*)], 6.83 [AA′ part of an AA′BB′ system, 2 H, 1,4-H, (*Z*)], 6.95 [td, ^3J = 7.8, ^4J = 1.0 Hz, 2 H, 2,6-H, (*E*)], 7.02 [BB′ part, 2 H, 2,3-H, (*Z*)], 7.09−7.27 [m, overlapping signals of (*E*)- and (*Z*)-**4b**], 7.18 [s, methine-H, (*Z*)], 7.24 [s, methine-H, (*E*)], 7.39 [AA′ part of an AA′BB′ system, 2 H, 6,7-H, (*Z*)], 7.79 [bd, ^3J = 7.8 Hz, 4,8-H, (*E*)], 7.84 [BB′ part, 2 H, 5,8-H, (*Z*)], due to overlap not all signals for (*E*)-**4b** could be found and not all integrals be determined. − ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 20.05 [q, CH$_3$, (*E*)], 20.12 [q, CH$_3$, (*Z*)], 123.40 [d, (*Z*)], 123.70 [d, (*E*)], 125.67 [d, (*E*)], 125.74 [d, (*Z*)], 125.98 [d, (*E*)], 126.12 [d, (*Z*)], 126.17 [d, (*Z*)], 127.16 [d, (*Z*)], 127.37 [d, (*Z*)], 127.40 [d, (*E*)], 128.02 [d, (*E*)], 128.11 [d, (*Z*)], 129.55 [d, (*Z*)], 129.64 [d, (*E*)], 130.11 [d, (*E*)], 130.15 [d, (*Z*)], 132.59 [s, (*E*)], 134.48 [s, (*Z*)], 135.92 [s, (*E*)], 135.98 [s, (*Z*)], 136.30 [s, (*Z*)], 136.34 [s, (*E*)], 136.57 [s, (*Z*)], 137.10 [s, (*E*)], 137.17 [s, (*Z*)], 138.51 [s, (*E*)], due to overlap not all signals for (*E*)-**4b** could be found. − $C_{30}H_{24}$ (384.5): calcd. C 93.71, H 6.29; found C 93.46, H 5.98.

(Z)-9,10-Bis(4′-methylphenylmethylene)-9,10-dihydroanthracene [(*Z*)-**4c**]: Compound (*Z*)-**4c** was prepared from 2-bromo-4′-methyl-*trans*-stilbene (*trans*-**7c**) (546 mg, 2.0 mmol) in a similar manner as that described for (*Z*)-**4a**, giving (*Z*)-**4c** (288 mg, 75%) as a pale-

yellow powder. M.p. 201−202°C. − UV (acetonitrile): λ_{max} (lg ε) = 223 nm (4.756), 245 (sh, 4.3), 338 (br., 4.409). − ^{1}H NMR ($CDCl_3$): δ = 2.37 (s, 6 H, 2 × CH_3), 6.98 (AA′ part of an AA′BB′ system, 2 H, 1,4-H), 7.08 (s, 2 H, methine-H), 7.14 (d, ^{3}J = 8.0 Hz, 4 H, 2′,6′-H), 7.30−7.43 (m, 8 H, 3′,5′,2,3,6,7-H), 7.81 (AA′ part of an AA′BB′ system, 2 H, 5,8-H). − ^{13}C NMR ($CDCl_3$): δ = 21.29 (q, CH_3) 123.07, 126.23, 127.07, 128.49 (all d, C-1,2,3,4,5,6,7,8), 126.68 (d, methine-C), 128.99, 129.31 (all d, C-2′,6′,3′,5′), 134.49, 134.91, 135.04, 136.88 (all s, C-1′,4′,4a,8a,9a,10a,9,10). − MS (70 eV, EI); *m/z* (%): 384 (100) [M^+], 382 (22), 352 (14), 279 (20), 265 (5), 176 (17), 169 (7). − $C_{30}H_{24}$ (384.5): calcd. C 93.71, H 6.29; found C 93.88, H 6.24.

(E/Z)-9,10-Bis(4′-methylphenylmethylene)-9,10-dihydroanthracene [(*E*/*Z*)-**4c**]: From a reaction of 2-bromo-4′-methyl-*trans*-stilbene (*trans*-**7c**) (1.092 g, 4.0 mmol) with K_2CO_3 (2.764 g, 20.0 mmol), LiCl (254 mg, 6.0 mmol), *n*Bu_4NBr (1.288 g, 4.0 mmol), and $Pd(OAc)_2$ (90 mg, 0.4 mmol), carried out as above, was obtained 748 mg (97%) of crude product after filtration through 30 g of flash silica gel eluting with pentane/CH_2Cl_2 (10:1). According to its ^{1}H- and ^{13}C-NMR spectra it was a 1:2.5 mixture of (*E*) and (*Z*) isomers. Crystallization from hexane gave 485 mg (63%) of pure (*Z*)-**4c**, and 258 mg of a 5:1 mixture of (*E*)-**4c** and (*Z*)-**4c**. − ^{1}H NMR (500 MHz, HH-COSY, $CDCl_3$): δ = 2.33 (s, 6 H, CH_3), 7.01 (dt, ^{3}J = 7.6, ^{4}J = 1.2 Hz, 2 H, 2,6-H), 7.06 (d, ^{3}J = 7.7 Hz, 4 H, 2′,6′-H), 7.11 (s, 2 H, methine-H), 7.26 (dt, ^{3}J = 7.6, ^{4}J = 1.2 Hz, 2 H, 3,7-H), 7.29 (d, ^{3}J = 7.7 Hz, 4 H, 3′,5′-H), 7.42 (dd, ^{3}J = 7.6, ^{4}J = 1.2 Hz, 2 H, 1,5-H), 7.77 (dd, ^{3}J = 7.5, ^{4}J = 1.0 Hz, 2 H, 4,8-H). − ^{13}C NMR ($CDCl_3$): δ = 21.27 (q, CH_3), 123.65, 125.67, 127.49, 128.18 (all d, C-1,2,3,4,5,6,7,8), 126.56 (d, methine-C), 128.93 (d, C-3′,5′), 129.23 (d, C-2′,6′), 132.51, 134.42, 134.96, 136.86, 139.26 (all s, C-1′,4′,4a,8a,9a,10a,9,10).

(E/Z)-9,10-Bis(4′-methoxyphenylmethylene)-9,10-dihydroanthracene [(*E*/*Z*)-**4d**]: Compound (*E*/*Z*)-**4d** (*E*/*Z* = 1:2) was prepared from 2-bromo-4′-methoxy-*trans*-stilbene (*trans*-**7d**) (578 mg, 2.0 mmol) in a similar manner as described for (*Z*)-**4a,** giving (*E*/*Z*)-**4d** (291 mg, 70%) as a pale-yellow powder. M.p. 136−137°C. − UV (acetonitrile): λ_{max} (lg ε) = 226 nm (4.741), 245 (sh), 341 (br., 4.418). − ^{1}H NMR (500 MHz, HH-COSY, $CDCl_3$): δ = 3.82 [s, 3 H, OCH_3, (*E*)-**4d**], 3.84 (s, 3 H, OCH_3, (*Z*)-**4d**], 6.79 [AA′ part of an AA′BB′ system, 4 H, 3′-H, (*E*)], 6.84 [AA′ part of an AA′BB′ system, 4 H, 3′-H, (*Z*)], 6.97 [AA′ part of an AA′BB′ system, 2 H, 1,4-H, (*Z*)], 7.01 [dt, ^{3}J = 8, ^{4}J = 2 Hz, B part of an ABCD system, 2 H, 2,6-H, (*E*)], 7.02 [s, 2 H, methine-H, (*Z*)], 7.07 [s, 2 H, methine-H, (*E*)], 7.27 [dt, ^{3}J = 8, ^{4}J = 2 Hz, C part, 2 H, 3,7-H, (*E*)], 7.32 [BB′ part, 2 H, 6,7-H, (*Z*)], 7.33 [BB′ part, 4 H, 2′-H, (*E*)], 7.39 [BB′ part, 4 H, 2′-H, (*Z*)], 7.42 [BB′ part, 2 H, 2,3-H, (*Z*)], 7.43 [dd, ^{3}J = 8, ^{4}J = 2 Hz, A part, 2 H, 1,5-H, (*E*)], 7.75 [dd, ^{3}J = 8, ^{4}J = 2 Hz, D part, 2 H, 4,8-H, (*E*)], 7.77 [AA′ part of an AA′BB′ system, 2 H, 5,8-H, (*Z*)]. − ^{13}C NMR ($CDCl_3$): δ = 55.21 (q), 113.63 (d), 113.71 (d), 123.02 (d), 123.62 (d), 125.62 (d), 126.13 (d), 126.21 (d), 126.24 (d), 126.99 (d), 127.45 (d), 128.07 (d), 128.46 (d), 129.74 (s), 129.79 (s), 130.61 (d), 130.68 (d), 132.57 (s), 134.25 (s), 135.02 (s), 136.93 (s), 139.41 (s), 158.71 (s). − MS (70 eV, EI); *m/z* (%): 416 (100) [M^+], 401 (5) [M^+ − Me], 297 (10) [M^+ − C_8H_7O]. − $C_{30}H_{24}O_2$ (416.5): calcd. C 86.51, H 5.81; found C 86.47, H 5.72.

(Z)-9,10-Bis(3′,5′-di-tert-butylphenylmethylene)-9,10-dihydroanthracene [(*Z*)-**4e**]: Compound (*Z*)-**4e** was prepared from 2-bromo-3′,5′-di-*tert*-butyl-*trans*-stilbene (*trans*-**7e**) (742 mg, 2.0 mmol) in a similar manner as described for (*Z*)-**4a**, giving (*Z*)-**4e** (290 mg, 50%) as a pale-yellow powder. M.p. 130−131°C. − UV (acetonitrile): λ_{max} (lg ε) = 223 nm (4.707), 245 (sh, 4.4), 332 (4.409). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (s, 36 H, 12 × CH_3), 6.93 (AA′ part of an AA′BB′ system, 2 H, 1,4-H), 7.11 (s, 2 H, methine-H), 7.26 (t, ^{3}J = 1.8 Hz, 2 H, 4′-H), 7.33 (BB′ part, 2 H, 6,7-H), 7.359 and 7.361 (2 d, ^{4}J = 1.8 Hz, 4 H, 2′,6′-H), 7.45 (BB′ part, 2 H, 2,3-H), 7.83 (AA′ part of an AA′BB′ system, 2 H, 5,8-H). − ^{13}C NMR ($CDCl_3$): δ = 31.47 (q), 34.78 (s), 120.98 (d), 123.25 (d), 123.95 (d), 126.12 (d), 127.00 (d), 127.70 (d), 128.61 (d), 134.74 (s), 134.80 (s), 136.25 (s), 137.06 (s), 150.35 (s). − MS (70 eV, EI); *m/z* (%): 580 (90) [M^+], 379 (3), 275 (10), 57 (100) [*t*Bu^+]. − $C_{44}H_{52}$ (580.9): calcd. C 90.98, H 9.02; found C 90.88, H 9.20.

(E/Z)-9,10-Bis(4′-methoxycarbonylphenylmethylene)-9,10-dihydroanthracene [(*E*/*Z*)-**4f**]: Compound (*E*/*Z*)-**4f** (*E*/*Z* = 1:1) was prepared from 2-bromo-4′-methoxycarbonyl-*trans*-stilbene (*trans*-**7f**) (634 mg, 2.0 mmol) in a similar manner as described for (*Z*)-**4a**, giving (*E*/*Z*)-**4f** (340 mg, 72%) as a pale-yellow powder. M.p. 172−173°C. − UV (acetonitrile): λ_{max} (lg ε) = 216 nm (4.656), 245 (sh, 4.4), 328 (4.469), 346 (4.463). − ^{1}H NMR ($CDCl_3$): δ = 3.91 (s, 6 H, 2 × Me), 3.93 (s, 6 H, 2 × Me), 6.98 [AA′ part of an AA′BB′ system, 2 H, 1,4-H, (*Z*)-**4f**], 7.04 (t, ^{3}J = 7.5 Hz, 2 H), 7.11 [s, 2 H, methine-H, (*Z*)], 7.18 [s, 2 H, methine-H, (*E*)-**4f**], 7.29−7.32 (m, 4 H), 7.36 (m, 2 H), 7.39 [BB′ part, 2 H, 2,3-H, (*Z*)], 7.47 (d, ^{3}J = 8.4 Hz, 4 H), 7.51 (d, ^{3}J = 8.4 Hz, 4 H), 7.79−7.82 (m, 4 H), 7.95 (d, ^{3}J = 8.3 Hz, 4 H), 8.01 (d, ^{3}J = 8.3 Hz, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 51.97 (q), 51.99 (q), 123.18 (d), 123.79 (d), 125.73 (d), 125.81 (d), 126.29 (d), 126.89 (d), 127.63 (d), 128.09 (d), 128.24 (d), 128.55 (s), 128.57 (s), 128.61 (d), 129.25 (d), 129.31 (d), 129.51 (d), 129.59 (d), 131.81 (s), 134.19 (s), 136.25 (s), 137.13 (s), 137.24 (s), 138.64 (s), 142.21 (s), 166.77 (C=O). − MS (70 eV, EI); *m/z* (%): 472 (50) [M^+], 413 (10) [M^+ − CO_2Me], 353 (20), 325 (12) [M^+ − $C_9H_7O_2$], 57 (100). − $C_{32}H_{24}O_4$ (472.5): calcd. C 81.34, H 5.12; found C 81.39, H 5.09.

(E/Z)-9,10-Bis(4′-nitrophenylmethylene)-9,10-dihydroanthracene [(*E*/*Z*)-**4g**]: Compound (*E*/*Z*)-**4g** (*E*/*Z* = 1.8:1) was prepared from 2-bromo-4′-nitro-*trans*-stilbene (*trans*-**7g**) (608 mg, 2.0 mmol) in a similar manner as described for (*Z*)-**4a**, giving (*E*/*Z*)-**4g** (250 mg, 56%) as a red powder. M.p. > 250°C. − UV (acetonitrile): λ_{max} (lg ε) = 215 nm (4.595), 260 (4.585), 358 (4.225), 376 (4.223), 397 (4.135). − ^{1}H NMR (500 MHz, HH-COSY, $CDCl_3$): δ = 7.04 [AA′ part of an AA′BB′ system, 2 H, 1,4-H, (*Z*)-**4g**], 7.08 [dt, ^{3}J = 8, ^{4}J = 2 Hz, 2 H, 2,6-H, (*E*)-**4g**], 7.12 [s, 2 H, methine-H, (*Z*)], 7.17 [s, 2 H, methine-H, (*E*)], 7.28 [d, ^{3}J = 8 Hz, 2 H, 1,5-H, (*E*)], 7.29 [BB′ part, 2 H, 2,3-H, (*Z*)], 7.36 [dt, ^{3}J = 8, ^{4}J = 2 Hz, 2 H, 3,7-H, (*E*)], 7.43 [AA′ part of an AA′BB′ system, 2 H, 6,7-H, (*Z*)], 7.53 [AA′ part of an AA′BB′ system, 4 H, 2′,6′-H, (*E*)], 7.58 [AA′ part of an AA′BB′ system, 4 H, 2′-H, (*Z*)], 7.82 [d, ^{3}J = 8 Hz, 2 H, 4,8-H, (*E*)], 7.83 [BB′ part, 2 H, 5,8-H, (*Z*)], 8.12 [BB′ part, 4 H, 3′,5′-H, (*E*)], 8.19 [BB′ part, 4 H, 3′,5′-H, (*Z*)]. − ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 123.38 (d), 123.70 (d), 123.82 (d), 124.08 (d), 124.71 (d), 124.79 (d), 126.90 (d), 127.60 (d), 128.21 (d), 128.27 (d), 128.71 (d), 128.77 (d), 130.09 (d, 2 C), 131.39 (s), 133.86 (s), 135.90 (s), 138.41 (s), 138.54 (s), 138.59 (s), 144.28 (s), 144.32 (s), 146.58 (s), 146.61 (s). − MS (70 eV, EI); *m/z* (%): 446 (100) [M^+], 416 (12) [M^+ − NO], 399 (8) [M^+ − HNO_2], 352 (20) [M^+ − 2 × HNO_2], 310 (10) [M^+ − $C_7H_6NO_2$]. − $C_{28}H_{18}N_2O_4$ (446.5): calcd. C 75.33, H 4.06, N 6.27; found C 75.30, H 4.01, N 6.25.

(E/Z)-9,10-Bis(2′-furylmethylene)-9,10-dihydroanthracene [(*E*/*Z*)-**4h**]: Compound (*E*/*Z*)-**4h** (*E*/*Z* = 1:1) was prepared from 1-bromo-2-(*trans*-2′-furylvinyl)benzene (*trans*-**7h**) (498 mg, 2.0 mmol) in a similar manner as described for (*Z*)-**4a**, giving (*E*/*Z*)-**4h** (255 mg, 76%) as a red oil. − UV (acetonitrile): λ_{max} (lg ε) = 229 nm (4.474), 256 (4.387), 326 (4.117), 374 (4.204). − ^{1}H NMR ($CDCl_3$): δ = 6.41−6.44 [m, 4 H, 1,4-H, (*Z*), 1,5-H, (*E*)], 6.61 [d,

^3J = 3.4 Hz, 2 H, furyl-3-H, (*E*)*], 6.67 [dd, ^3J = 2.8, ^4J = 0.5 Hz, 2 H, furyl-3-H, (*Z*)*], 6.85 [s, 2 H, methine-H, (*Z*)], 6.91 [s, 2 H, methine-H, (*E*)], 7.25−7.42 (m, 12 H), 7.72−7.78 (m, 4 H), 7.92 [dd, ^3J = 7.7, ^4J = 1.4 Hz, 4,8-H, (*E*)], 7.96 [AA′ part of an AA′BB′ system, 5,8-H, (*Z*)]. − ^{13}C NMR ($CDCl_3$): δ = 110.76 (d), 110.82 (d), 111.54 (d), 114.68 (d), 114.83 (d), 122.91 (d), 123.22 (d), 125.73 (d), 126.59 (d), 127.18 (d), 127.84 (d), 127.98 (d), 129.19 (d), 132.48 (s), 133.43 (s), 134.47 (s), 136.98 (s), 139.11 (s), 141.93 (d), 141.96 (d), 152.11 (s), 152.24 (s). − MS (70 eV, EI); *m/z* (%): 336 (100) [M^+], 307 (13) [M^+ − HCO], 276 (15), 252 (17). − $C_{24}H_{16}O_2$: calcd. 336.11503, found 336.11502 (MS).

(E/Z)-2,6-Bis(ethoxycarbonyl)-9,10-bis(phenylmethylene)-9,10-dihydroanthracene [(*E*/*Z*)-**4j**]: Compound (*E*/*Z*)-**4j** (*E*/*Z* = 1:1.1) was prepared from 2-bromo-5-(ethoxycarbonyl)-*trans*-stilbene (*trans*-**7j**) (662 mg, 2.0 mmol) in a similar manner as described for (*Z*)-**4a**, giving (*E*/*Z*)-**4j** (390 mg, 78%) as a pale-yellow powder. M.p. 201−202°C. − UV (acetonitrile): λ_{max} (lg ε) = 211 nm (4.627), 258 (4.648), 323 (3.775). − ^{1}H NMR ($CDCl_3$): δ = 1.20 [t, ^3J = 7 Hz, 3.3 H, CH_3, (*Z*)], 1.23 [t, ^3J = 7 Hz, 3.3 H, CH_3, (*Z*)], 1.47 [t, ^3J = 7 Hz, 6 H, CH_3, (*E*)], 4.21 [q, ^3J = 7 Hz, 2.2 H, CH_2O, (*Z*)], 4.23 [q, ^3J = 7 Hz, 2.2 H, CH_2O, (*Z*)], 4.47 [q, ^3J = 7 Hz, 4 H, CH_2O, (*E*)], 7.25−7.47 (m, 30 H), 7.64 (dd, ^3J = 8.2, ^4J = 1.7 Hz, 2.2 H), 7.86 (dd, ^3J = 8.2, ^4J = 1.1 Hz, 2.2 H), 7.96−8.08 (m, 5 H), 8.50 (d, ^4J = 1.6 Hz, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 14.04 (q), 14.37 (q), 60.66 (t), 61.09 (t), 123.35 (d), 123.87 (d), 124.71 (d), 127.20 (d), 127.66 (d), 127.72 (d), 128.10 (d), 128.36 (d), 128.41 (d), 128.45 (d), 128.64 (d), 129.07 (d), 129.15 (d), 129.18 (d), 129.25 (d), 129.36 (d), 129.42 (d), 129.86 (d), 130.06 (d), 131.90 (s), 134.25 (s), 134.30 (s), 134.32 (s), 136.42 (s), 136.53 (s), 136.55 (s), 136.65 (s), 138.83 (s), 140.49 (s), 142.63 (s), 165.94 (C=O), 165.98 (C=O), 166.33 (C=O). − MS (70 eV, EI); *m/z* (%): 500 (50) [M^+], 427 (3) [M^+ − CO_2Et], 353 (10), 350 (12). − $C_{34}H_{28}O_4$ (500.6): calcd. C 81.58, H 5.64; found C 81.39, H 5.53.

(E/Z)-2,6-Bis(methoxycarbonyl)-9,10-bis(4′-methoxyphenylmethylene)-9,10-dihydroanthracene [(*E*/*Z*)-**4k**]: Compound (*E*/*Z*)-**4k** (*E*/*Z* = 2:3) was prepared from 2-bromo-5-methoxycarbonyl-4′-methoxy-*trans*-stilbene (*trans*-**7k**) (694 mg, 2.0 mmol) in a similar manner as described for (*Z*)-**4a**, giving (*E*/*Z*)-**4k** (340 mg, 64%) as a pale-yellow powder. M.p. 159−160°C. − UV (acetonitrile): λ_{max} (lg ε) = 242 nm (4.777), 272 (sh, 4.4), 363 (br., 4.447). − ^{1}H NMR ($CDCl_3$): δ = 3.77 [s, 3 H, Me, (*Z*)], 3.79 [s, 3 H, Me, (*Z*)], 3.81 [s, 4 H, Me, (*E*)], 3.83 [s, 3 H, Me, (*Z*)], 3.84 [s, 4 H, Me, (*E*)], 3.97 (s, 3 H, Me, (*Z*)], 6.79 [d, ^3J = 8.7 Hz, 2.7 H, 3′,5′-H, (*E*)], 6.85 [dd, ^3J = 8.8, ^4J = 2.9 Hz, 4 H, 3′,5′-H, (*Z*)], 7.12 [s, 1 H, methine-H, (*Z*)], 7.17 [s, 1.3 H, methine-H, (*E*)], 7.18 [s, 1 H, methine-H, (*Z*)], 7.32 [d, ^3J = 8.7, ^4J = 2.7 Hz, 2.7 H, 2′,6′-H, (*E*)], 7.38 [dd, ^3J = 8.8, ^4J = 2.2 Hz, 4 H, 2′,6′-H, (*Z*)], 7.50 [d, ^3J = 8.3 Hz, 1 H, 4-H, (*Z*)], 7.65 [dd, ^3J = 8.3, ^4J = 1.7 Hz, 1 H, 3-H, (*Z*)], 7.78 [d, ^3J = 7.7 Hz, 1.3 H, 4-H, (*E*)], 7.82 [d, ^3J = 8.2 Hz, 1 H, 8-H, (*Z*)], 7.94 [d, ^3J = 7.7 Hz, 1.3 H, 3-H, (*E*)], 7.98 [dd, ^3J = 8.3, ^4J = 1.7 Hz, 1 H, 7-H, (*Z*)], 8.14 [d, ^4J = 1.5 Hz, 1.3 H, 1-H, (*E*)], 8.15 [d, ^4J = 1.5 Hz, 1 H, 1-H, (*Z*)], 8.44 [d, ^4J = 1.6 Hz, 1 H, 5-H, (*Z*)]. − ^{13}C NMR ($CDCl_3$): δ = 51.82 (q), 52.04 (q), 55.12 (q), 113.83 (d), 113.90 (d), 123.13 (d), 123.78 (d), 124.52 (d), 127.09 (d), 127.52 (d), 128.07 (d), 128.50 (d), 128.56 (d), 128.62 (d), 128.67 (d), 128.76 (d), 128.84 (d), 128.86 (d), 128.92 (d), 129.46 (d), 129.81 (d), 130.48 (d), 130.59 (d), 130.70 (d), 132.25 (s), 132.64 (s), 132.77 (s), 134.73 (s), 136.53 (s), 139.34 (s), 141.01 (s), 143.36 (s), 159.20 (s), 159.28 (s), 166.51 (C=O), 166.54 (C=O), 166.81 (C=O). − MS (70 eV, EI); *m/z* (%): 532 (40) [M^+], 413 (5) [M^+ − C_8H_7O], 355 (10), 339 (18), 326 (30), 135 (40) [$C_8H_7O_2^+$], 59 (100) [CO_2Me^+]. − $C_{34}H_{28}O_6$ (532.6): calcd. C 76.68, H 5.30; found C 76.66, H 5.44.

Palladium-Catalyzed Intramolecular Cyclization of 2-Bromo-cis-stilbenes

3-Methylphenanthrene (**12c**): A mixture of 2-bromo-4′-methyl-*cis*-stilbene (*cis*-**7c**) (546 mg, 2.0 mmol), K_2CO_3 (1.4 g, 10 mmol), LiCl (127 mg, 3.0 mmol), *n*Bu_4NBr (644 mg, 2.0 mmol), and $Pd(OAc)_2$ (45 mg, 0.2 mmol) in DMF (20 ml) was heated in a sealed tube at 110°C for 15 h. After addition of ice/water (200 ml) and cooling to room temperature, the mixture was extracted with diethyl ether (2 × 100 ml). The combined organic solutions were washed with water (2 × 100 ml), dried ($MgSO_4$) and concentrated. Purification by column chromatography (SiO_2, 100 g, pentane) yielded 3-methylphenanthrene (272 mg, 71%) as colorless needles. M.p. 102−104°C. − ^{1}H NMR ($CDCl_3$): δ = 2.64 (s, 3 H, Me), 7.44 (d, ^3J = 8.1 Hz, 1 H), 7.61 (dt, ^3J = 8.4, ^4J = 0.4 Hz, 2 H), 7.69 (d, ^4J = 2.5 Hz, 2 H), 7.79 (d, ^3J = 8.1 Hz, 1 H), 7.89 (dd, ^4J = 1.7, ^5J = 0.7 Hz, 1 H), 8.49 (s, 1 H), 8.68 (d, ^3J = 7.9 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 22.13 (q), 122.40 (d), 122.62 (d), 125.95 (d), 126.31 (d), 126.40 (d), 126.72 (d), 128.29 (d), 128.40 (d), 128.52 (d), 130.04 (s), 130.35 (s), 136.27 (s). − MS (70 eV, EI); *m/z* (%): 192 (100) [M^+]. − $C_{15}H_{12}$ (192.3): calcd. C 93.71, H 6.29; found C 93.70, H 6.21.

Phenanthrene (**12a**): According to the above procedure for a palladium-catalyzed intramolecular cyclization, phenanthrene (249 mg, 70%) was obtained as colorless crystals from 2-bromo-*cis*-stilbene (*cis*-**7a**) (518 mg, 2.0 mmol).

Palladium-Catalyzed Reductions of 2-Bromo-cis-stilbenes

4′-Methoxycarbonyl-cis- and -trans-stilbene: A mixture of 2-bromo-4′-methoxycarbonyl-*cis*-stilbene (*cis*-**7f**) (634 mg, 2.0 mmol), $Pd(PPh_3)_4$ (69 mg, 0.06 mmol), NaOMe (112 mg, 2.1 mmol), and Et_3N (30 ml) was heated under reflux until the starting material had disappeared (approx. 24 h). After removal of the solvent, the residue was purified by column chromatography (SiO_2, 200 g, pentane/CH_2Cl_2, 20:1) to yield 4′-methoxycarbonyl-*cis*-and -*trans*-stilbene (1:1, 333 mg, 70%). − *4′-Methoxycarbonyl-cis-stilbene:* Colorless oil. − ^{1}H NMR ($CDCl_3$): δ = 3.90 (s, 3 H, OMe), 6.61 (d, ^3J = 12.3 Hz, 1 H), 6.72 (d, ^3J = 12.3 Hz, 1 H), 7.23 (s, 5 H), 7.31 (d, ^3J = 8.0 Hz, 2 H), 7.90 (d, ^3J = 8.0 Hz, 2 H). − MS (70 eV, EI); *m/z* (%): 238 (100) [M^+], 207 (45) [M^+ − OMe], 179 (70) [M^+ − CO_2Me]. − $C_{16}H_{14}O_2$ (238.3): calcd. C 80.65, H 5.92; found C 80.63, H 5.89. − *4′-Methoxycarbonyl-trans-stilbene:* Colorless oil. − ^{1}H NMR ($CDCl_3$): δ = 3.88 (s, 3 H, OMe), 6.72 (s, 2 H), 7.09−7.11 (m, 3 H), 7.19 (d, ^3J = 8.3 Hz, 2 H), 7.60−7.63 (m, 1 H), 7.85 (d, ^3J = 8.3 Hz, 2 H). − MS (70 eV, EI); *m/z* (%): 238 (100) [M^+], 207 (40) [M^+ − OMe], 179 (80) [M^+ − CO_2Me]. − $C_{16}H_{14}O_2$ (238.3): calcd. C 80.65, H 5.92; found C 80.61, H 5.95.

3′,5′-Di-tert-butyl-cis- and -trans-stilbene: According to the above procedure, 3′,5′-di-*tert*-butyl-*cis*- and -*trans*-stilbene were obtained as a colorless oil (1:1, 380 mg, 65%) from 2-bromo-(3′,5′-di-*tert*-butyl)-*cis*-stilbene (*cis*-**7e**) (742 mg, 2.0 mmol). − *3′,5′-Di-tert-butyl-cis-stilbene:* ^{1}H NMR ($CDCl_3$): δ = 1.24 (s, 18 H, 6 × Me), 6.62 (s, 2 H), 7.13 (d, ^3J = 1.5 Hz, 2 H), 7.23−7.33 (m, 6 H). − ^{13}C NMR ($CDCl_3$): δ = 31.31 (q), 34.67 (s), 121.03 (d), 123.44 (d), 126.88 (d), 128.15 (d), 128.85 (d), 129.57 (d), 131.31 (d), 136.04 (s), 137.87 (s), 150.36 (s). − MS (70 eV, EI); *m/z* (%): 292 (100) [M^+], 277 (60) [M^+ − Me], 57 (65) [*t*Bu^+]. − $C_{22}H_{28}$ (292.5): calcd. C 90.35, H 9.65; found C 90.31, H 9.63. − *3′,5′-Di-tert-butyl-trans-stilbene:* Colorless oil. − ^{1}H NMR ($CDCl_3$): δ = 1.39 (s, 18 H, 6 × Me), 7.14 (d, ^3J = 5.2 Hz, 2 H), 7.26−7.39 (m, 6 H), 7.56 (d, ^3J = 7.3 Hz, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 31.48 (q), 34.87 (s), 120.86 (d), 122.11 (d), 126.45 (d), 127.35 (d), 128.03 (d), 128.62 (d), 129.90 (d), 136.56 (s), 137.71 (s), 151.06 (s). − MS (70 eV, EI); *m/z*

(%): 292 (100) [M$^+$], 277 (55) [M$^+$ − Me], 57 (30) [tBu$^+$]. − $C_{22}H_{28}$ (292.5): calcd. C 90.35; H 9.65; found C 90.31, H 9.63.

According to the above procedure, *cis*/*trans*-stilbene (4:3, 250 mg, 70% yield) and 4′-methyl-*cis*- and -*trans*-stilbene (1:1, 271 mg, 70% yield) were obtained from 2-bromo-*cis*-stilbene (*cis*-**7a**) (518 mg, 2.0 mmol) and 2-bromo-4′-methyl-*cis*-stilbene (*cis*-**7c**) (546 mg, 2.0 mmol), respectively.

Cross-Over Experiment for the Palladium-Catalyzed Reaction of 2-Bromo-trans-stilbene (*trans*-**7a**) *and 2-Bromo-5-ethoxycarbonyl-trans-stilbene* (*trans*-**7j**): A mixture of 2-bromo-*trans*-stilbene (*trans*-**7a**) (259 mg, 1.0 mmol), 2-bromo-5-ethoxycarbonyl-*trans*-stilbene (*trans*-**7j**) (331 mg, 1.0 mmol), K_2CO_3 (1.4 g, 10 mmol), LiCl (254 mg, 6.0 mmol), nBu$_4$NBr (644 mg, 2.0 mmol), and Pd(OAc)$_2$ (45 mg, 0.2 mmol) in DMF (30 ml) was heated in a sealed tube at 110°C for 24 h. After addition of ice/water (200 ml) and cooling to room temperature, the mixture was extracted with diethyl ether (3 × 100 ml). The combined organic solutions were washed with water (4 × 100 ml), dried (MgSO$_4$), and concentrated. Purification by column chromatography (SiO$_2$, 200 g, pentane/ethyl acetate, 15:1) yielded (*Z*)-**4a** (107 mg, 30%), (*E*/*Z*)-**4j** (100 mg, 20%), and inseparable cross-coupling products (*Z*)-6-(ethoxycarbonyl)-9,10-bis(phenylmethylene)-9,10-dihydroanthracene [(*Z*)-**22**], (*Z*)-2-(ethoxycarbonyl)-9,10-bis(phenylmethylene)-9,10-dihydroanthracene [(*Z*)-**23**], and (*E*)-2-(ethoxycarbonyl)-9,10-bis(phenylmethylene)-9,10-dihydroanthracene [(*E*)-**23**] (86 mg, 20%). Pale-yellow powder, m.p. 172−173°C. − ^{1}H NMR (CDCl$_3$): δ = 1.18−1.30 (m, 7.3 H, CH$_3$), 1.47 (t, ^3J = 7.1 Hz, 4.0 H, CH$_3$), 4.19 and 4.22 (2 q, ^3J = 7 Hz, 2.2 H, 2 × OCH$_2$), 4.46 (q, ^3J = 7.1 Hz, 2.4 H, OCH$_2$), 7.00 (AA′ part of an AA′BB′ system, 2.1 H), 7.18−7.60 (m, 37.4 H), 7.81−8.00 (m, 4.2 H), 8.03 (d, ^4J = 1.4 Hz, 1.7 H), 8.51 (d, ^4J = 1.4 Hz, 1.0 H). − MS (70 eV, EI); *m/z* (%): 428 (100) [M$^+$], 399 (4) [M$^+$ − Et], 352 (17) [M$^+$ − C$_6$H$_4$], 326 (10). − $C_{31}H_{24}O_2$: calcd. 428.1776, found 428.1776 (MS).

Cyclovoltammetry on 9,10-Dibenzylidene-9,10-dihydroanthracene [(*Z*)-**4a**]: The cyclovoltammograms were recorded with a potentiostat/galvanostat type Autolab PGSTAT 20 by ECO Chemie at a scan rate of 0.05 V/s for a $2 \cdot 10^{-4}$ M solution of (*Z*)-**4a** in anhydrous acetonitrile (Aldrich HPLC grade, dried over molecular sieves 3 Å), 0.1 M in nBu$_4$NPF$_6$ as a conducting salt. The conducting salt was prepared and purified according to published procedures[18]. Working electrode: glassy/carbon plate electrode (diameter 5.6 mm), counter electrode: platinum wire, reference electrode: silver/silver chloride in EtOH, saturated with LiCl.

☆ Dedicated to Professor *Heinz Georg Wagner* on the occasion of his 70th birthday.

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