Palladium-Catalyzed Cascade Reaction of α,β-Unsaturated Sulfones with Aryl Iodides

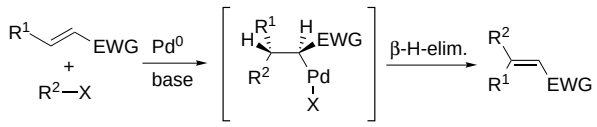
Pablo Mauleón, Angel A. Núñez, Inés Alonso, and Juan C. Carretero*[a]

Abstract: Unlike traditionally used acyclic 1,2-disubstituted alkenes, the reaction of α,β-unsaturated phenyl sulfones with aryl iodides under Heck reaction conditions ($Pd(OAc)_2$ as catalyst, Ag_2CO_3 as base in DMF at 120 °C) takes place mainly by a cascade process, involving one unit of the alkene and three units of the aryl iodide, to afford a substituted 9-phenylsulfonyl-9,10-dihydrophenanthrene. The dominant formation of this 3:1 coupling product, instead of the Heck trisubstituted olefin, shows that aromatic C–H activation processes can compete with the usually fast *syn* β-hydrogen elimination step in the Heck arylation of an acyclic olefin. The structural scope of this palladium-catalyzed cascade arylation of α,β-unsaturated sulfones has proved to be wide with regard to substitution at the β-position (alkyl, aryl, or alkenyl substitution), substitution at the sulfone unit (alkyl or phenyl sulfones), and configuration at the C=C bond (*trans* or *cis*). Moreover, although less favored than in the case of the arylation of α,β-unsaturated sulfones, similarly substituted 9,10-dihydrophenanthrenes have also been obtained in the case of α,β-unsaturated phosphine oxides and α,β-unsaturated phosphonate esters. A $Pd^0-Pd^{II}-Pd^{IV}$ mechanistic pathway involving the successive formation of highly electrophilic σ-alkylpalladium intermediates and palladacycles is proposed for this multicomponent arylation.

Keywords: C–H activation · domino reactions · Heck reaction · palladium · sulfones

Introduction

Since its discovery in the late 1960s,[1] the palladium-catalyzed arylation or vinylation of alkenes (the Heck reaction) has received increasing attention, becoming one of the most versatile and synthetically useful methods for C–C bond formation used today.[2] Owing to the high sensitivity of the Heck reaction to steric factors, the vast majority of the huge number of Heck reactions reported to date deal either with intramolecular versions of this reaction[3] or with intermolecular processes on terminal olefins and cycloalkenes.[2] In recent years, however, considerable progress has been achieved in the stereoselective synthesis of acyclic, trisubstituted olefins by Heck reaction of organic halides with 1,2-disubstituted olefins, in particular when electronically poor olefins like α,β-unsaturated carbonyl compounds[4] and α,β-unsaturated sulfoxides[5] are employed (Scheme 1).



Scheme 1. Synthesis of trisubstituted alkenes by Heck reaction. EWG = electron-withdrawing group = CO_2R, COR, CN, SOAr; R^1 = alkyl or aryl, R^2 = aryl or alkenyl.

As part of our ongoing research focused on the development of highly stereoselective methods with readily available functionalized α,β-unsaturated sulfones[6], we envisaged that acyclic β,β′-disubstituted, α,β-unsaturated sulfones could be stereoselectively prepared by simple Heck reactions of the corresponding β-substituted, α,β-unsaturated sulfone. In fact, Fuchs et al. have reported several examples of intramolecular Heck reactions of α,β-unsaturated sulfones.[7]

Contrary to these precedents, we describe herein that the intermolecular palladium-catalyzed reaction of β-substituted, α,β-unsaturated sulfones with a large excess of iodobenzene (or *p*-substituted iodoarenes), in the presence of Ag_2CO_3 as base, occurs mainly through a complex cascade reaction in which three molecules of iodobenzene and one molecule of vinyl sulfone are involved, affording 1-phenyl-9-phenylsulf-

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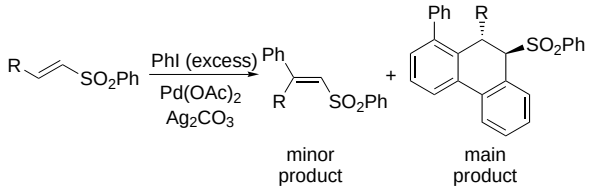
Supporting information for this article, including experimental procedures and spectroscopic and analytical data for all compounds not presented in the experimental section, is available on the WWW under http://www.chemeuj.org or from the author.

  0947-6539/03/0907-1511 $ 20.00+.50/0

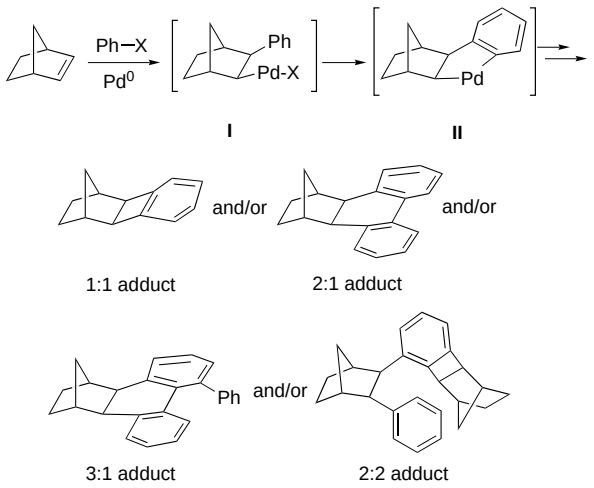
onyl-9,10-dihydrophenanthrenes, rather than the expected Heck trisubstituted olefin[8] (Scheme 2). The formation of this 3:1 coupling product, in which four C–C bonds are formed in a single synthetic step, indicates that *ortho* C–H activation processes[9] can compete favorably with the seemingly obvious final β-hydrogen elimination step of a Heck reaction.



Scheme 2. Palladium-catalyzed arylation of α,β-unsaturated sulfones.

As far as we know such a palladium catalyzed cascade arylation of an acyclic alkene has not been previously reported. The most comparable results were those described by the groups of Catellani and de Meijere in the palladium-catalyzed reactions of aryl halides with norbornene.[10] This very reactive bicyclic alkene has been widely used in interrupted Heck reactions and in a variety of cascade processes[11] because the final *syn* β-hydrogen elimination step is structurally not feasible. Thus, in this case the insertion step generates the long-lived σ-alkylpalladium intermediate (**I**) that, being unable to undergo β-hydrogen elimination, undergoes an intramolecular aromatic C–H activation process with formation of the key 5-membered palladacycle intermediate (**II**).[12] Depending on experimental conditions 1:1, 2:1, 3:1, or 2:2 coupling products are finally isolated[10] (Scheme 3).

Abstract in Spanish: *Al contrario de lo que ocurre con otros alquenos acíclicos 1,2-disustituidos, la reacción de Heck de fenil sulfonas α,β-insaturadas con yoduros de arilo [Pd(OAc)$_2$ como catalizador, Ag$_2$CO$_3$ como base en DMF a 120 °C] transcurre de forma mayoritaria a través de una reacción en cascada que implica la participación de una unidad de alqueno y tres de yoduro de arilo, dando lugar a 9-fenilsulfonil-9,10-dihidrofenantrenos. La formación de este producto de acoplamiento 3:1, en lugar de la olefina trisustituida, pone de manifiesto que procesos de activación aromática C–H pueden competir con la etapa de β-eliminación* syn, *normalmente rápida en procesos de arilación de Heck de olefinas acíclicas. Desde un punto de vista estructural esta reacción en cascada presenta un carácter muy general, teniendo lugar con sulfonas α,β-insaturadas portadoras de sustituyentes alquilo, arilo o alquenilo en posición β, sustituyentes alquilo o fenilo en la unidad de sulfona y configuración* trans *o* cis *en el doble enlace. Por otra parte, aunque menos favorecido que en el caso de las sulfonas, los óxidos de fosfina y los fosfonatos α,β-insaturados también conducen a la formación de 9,10-dihidrofenantrenos. Este proceso de arilación multicomponente puede explicarse a través de un ciclo catalítico que implica diversos estados de oxidación del paladio (Pd^0-Pd^{II}-Pd^{IV}) con formación sucesiva de intermedios σ-alquilpaladio altamente electrófilos y paladaciclos.*

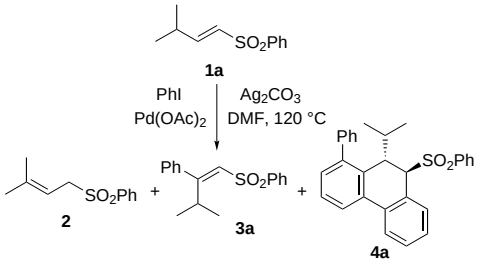


Scheme 3. Palladium-catalyzed arylation of norbornene.

Results and Discussion

Search for the optimal experimental conditions: When our model *trans*-substituted α,β-unsaturated sulfone **1a**[13] was treated with iodobenzene in the presence of Pd(OAc)$_2$ (10 mol %) as catalyst and K_2CO_3 or Cs_2CO_3 as base in DMF at 120 °C, we only detected the basic isomerization of the vinyl sulfone **1a** to the allyl sulfone **2.**[14] On the other hand, a sluggish reaction was observed using a typical mild base such as Et_3N. Therefore, we turned our attention to the use of Ag_2CO_3, a base which proved to be very effective in our previous studies of Heck reactions of α,β-unsaturated sulfoxides.[5] Under these conditions (Pd(OAc)$_2$ 10 mol %, Ag_2CO_3 200 mol %, DMF, 120 °C, 72 h) the reaction of **1a** with an equimolar amount of iodobenzene afforded a mixture of the starting vinyl sulfone **1a**, the allyl sulfone **2**, the expected Heck product **3a**, and, unexpectedly, the dihydrophenanthrene **4a** (Table 1, entry 1). In agreement with the fact that the formation of **4a** requires three units of iodobenzene, both the conversion of the reaction and the yield in dihydrophe-

Table 1. Palladium-catalyzed reaction of **1a** with iodobenzene.[a]



Entry	PhI (equiv)	**1a**:**2**:**3a**:**4a**[b]
1	1	23:30:26:21
2	5	8:5:6:81
3	10	1:–:5:94

[a] Reaction conditions: Ag_2CO_3 (200 mol %), Pd(OAc)$_2$ (10 mol %), DMF, 120 °C, 72 h, [**1a**] = 0.2 M. [b] Evaluated by ^{1}H NMR spectroscopy of the crude mixtures.

0947-6539/03/0907-1512 $ 20.00+.50/0 *Chem. Eur. J.* **2003**, *9*, No. 7

nanthrene **4a** were progressively enhanced with increasing amounts of iodobenzene[15] (Table 1, entries 1–3). In the presence of 10 equivalents of iodobenzene a clean reaction in favor of the formation of the domino product **4a** was observed (**3a**:**4a** = 5:95, 86% yield, Table 1, entry 3). A further recristallyzation from diethyl ether provided pure dihydrophenanthrene **4a** in 69% overall yield. The structural determination of **4a** was first undertaken by NMR and mass spectrometric studies and its unequivocal confirmation, including the *trans* stereochemistry at C-9/C-10, was established by X-ray crystallographic analysis[16] (Figure 1).

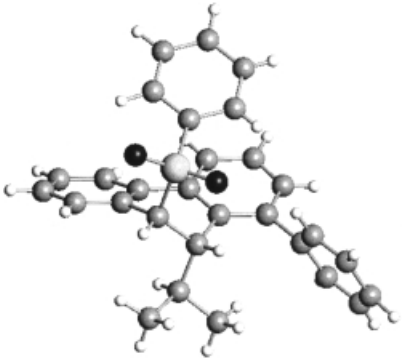
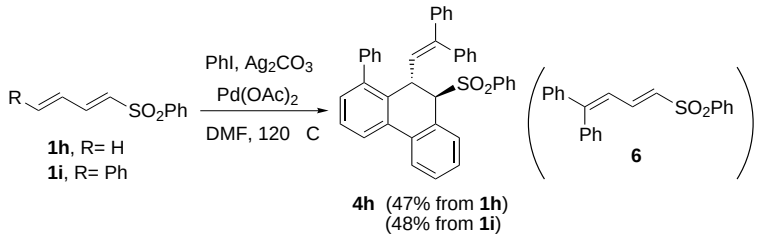


Figure 1. Crystal structure of compound **4a.**

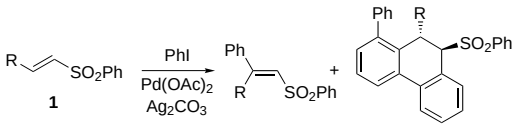
Scope of the cascade arylation of α,β-unsaturated phenyl sulfones: To determine the dependence of the reaction on the nature of the β-substituent of the α,β-unsaturated sulfone, a variety of *trans*-substituted α,β-unsaturated sulfones (substrates **1b**–**f**) were treated with iodobenzene under the best conditions previously found for **1a** (Scheme 4, Table 2). Interestingly, the results were rather homogeneous regardless



Scheme 4. Palladium-catalyzed reaction of dienyl sulfones with iodobenzene.

of the relatively varied steric and electronic properties of the substituent in the β-position. Thus, in most cases the cascade product **4** predominated largely over the Heck product **3** with both β-alkyl- (Table 2, entries 1, 3, and 4) and β-aryl substituted vinyl sulfones[13] (Table 2, entries 5 and 6). The only exception to this general trend was the behavior of the methyl-substituted vinyl sulfone **1b** (Table 2, entry 2). In this case a more complex mixture of products was obtained, the dihydrophenanthrene **4b** being detected in low yield (27% on the crude reaction mixture) along with the major formation of a mixture of monoarylated (**3b**) and diarylated Heck olefin products (**5**). The formation of **5** is most likely due to the high

Table 2. Palladium-catalyzed reaction of *trans*-α,β-unsaturated sulfones **1** with iodobenzene.[a]



Entry	Alkene	R	**3**:**4** [%][b]	Yield[c][%] (**4**[d][%])
1	**1a**	*i*Pr	**3a**:**4a** = 5:95	86 (69)
2	**1b**	Me	**3b**:**4b**:**5**[e] = 11:27:52	–[f]
3	**1c**	*n*Pent	**3c**:**4c** = 12:88	82[g]
4	**1d**	Cy	**3d**:**4d** = 10:90	84[g]
5	**1e**	Ph	**3e**:**4e** = 3:97	82 (63)
6	**1f**	β-Naph	**3f**:**4f** = 8:92	85 (61)
7[h]	**1g**	H	**3e**:**4e** = 4:96	78 (60)

[a] Reaction conditions: PhI (10 equiv), $Pd(OAc)_2$ (10 mol%), Ag_2CO_3 (200 mol%), DMF, 120 °C, 3–5 days. [b] Determined by ^1H NMR spectroscopy of the crude mixtures. [c] Yield in **3** + **4** after flash chromatography (compound **4** was only partially separated). [d] Yield of pure compound **4** after recrystallization. [e] Compound **5** = 1,2-diphenyl-3-(phenylsulfonyl)-1-propene. [f] Pure compound **4b** could not be separated by chromatography or recrystallization. [g] Dihydrophenanthrenes **4c** and **4d** could not be crystallized. About 10–15% of pure **4c** and **4d** were obtained after flash chromatography [toluene/iPr_2O (100:1)]. [h] 250 mol% of Ag_2CO_3 was used.

tendency of **1b**[17] (and probably **3b**) to undergo basic isomerization to the corresponding allyl phenyl sulfone and further Heck reaction on the C=C bond.

A particularly interesting result was obtained from the β-unsubstituted commercially available phenyl vinyl sulfone (**1g**, Table 2, entry 7), which afforded dihydrophenanthrene **4e** in high yield. This product is the same as that obtained in the reaction of the β-phenyl substituted substrate **1e** (Table 2, entry 5), showing that in the reaction of **1g** four molecules of iodobenzene were involved in the process, with the subsequent formation of five C–C bonds. This result can be readily explained by assuming that the β-unhindered vinyl sulfone **1g** first undergoes a very favorable Heck reaction to afford the sterically uncongested, *trans*-substituted olefin **1e**, which in the presence of an excess of iodobenzene reacts in situ by the cascade process to give the dihydrophenanthrene **4e**. In full agreement with this hypothesis, **1e** was isolated in high yield (82% after chromatographic purification) when the palladium-catalyzed reaction of **1g** was carried out in the presence of a stoichiometric amount of iodobenzene instead of a tenfold excess.

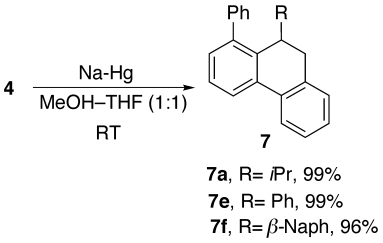
Although the mixture of products **3** and **4** could not, because of their very similar chromatographic mobilities, be completely separated by flash chromatography in any of the cases, pure compounds **4a**, **4e**, and **4f** were readily obtained by further recrystallization from diethyl ether (61–69% yields).[18] The structure of the dihydrophenanthrenes **4** was unequivocally established by NMR spectroscopic and mass

spectrometric studies,[19] and the structure of the 1,10-diphenyl dihydrophenanthrene **4e** was confirmed by X-ray crystallographic analysis.[16]

The study of the scope of this reaction was extended to the case of the vinylogous substrates: the 1-(phenylsulfonyl)-1,3-dienes **1h** and **1i** (Scheme 4). The behavior of this type of α,β-unsaturated sulfone was particularly interesting owing to the presence of two potentially reactive C=C bonds. Surprisingly, despite the different substitution at the terminal position of the diene, both compounds reacted similarly with excess of PhI/Ag_2CO_3 under the usual reaction conditions ($Pd(OAc)_2$, DMF, 120 °C) affording as the main product the same 9-(phenylsulfonyl)-9,10-dihydrophenanthrene **4h**[19] (47–48% yield of pure product after chromatographic purification and recrystallization). The structure of **4h** was unequivocally confirmed by X-ray crystallographic analysis.[16] This result clearly reveals the quite different reactivity of both types of C=C bonds of the diene unit. Thus, while the C3=C4 bond underwent a regioselective Heck arylation at C4 (or double Heck arylation in the case of **1h**), the α,β-unsaturated phenylsulfonyl moiety reacted according to the cascade arylation process. In terms of chemical complexity the behavior of **1h** is especially remarkable, since in this case the process involves the participation of five units of iodobenzene and the resulting formation of six C–C bonds.

From a mechanistic point of view it is interesting to note that when the reactions of **1h** and **1i** were performed, respectively, in the presence of two or one equivalents of PhI (instead of a large excess), the 4,4-diphenyldiene **6** was detected in both cases in the crude mixtures. This result suggests that **6** could be a common intermediate in the cascade arylation of **1h** and **1i**.

According with the structural assignment of compounds **4**, their reductive desulfonylation by treatment with Na-Hg (MeOH, THF, room temperature) led almost quantitatively to the corresponding 1-phenyl-10-substituted-9,10-dihydrophenanthrenes **7** (Scheme 5). From a synthetic point of view, it

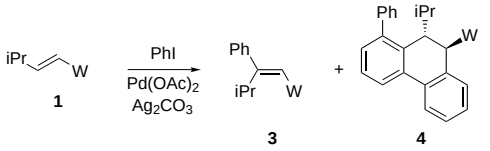


Scheme 5. Desulfonylation of compounds **4**.

should be noted that this two-step sequence, cascade arylation of α,β-unsaturated sulfones and further desulphonylation, constitutes an extremely convergent synthesis of 1-phenyl-substituted 9,10-dihydrophenanthrenes from a benzene derivative.

Reaction of other electron-deficient alkenes: Having demonstrated the general scope of the cascade palladium-catalyzed reaction of α,β-unsaturated phenyl sulfones with iodoarenes in the presence of Ag_2CO_3, it was important to determine if this competitive process to the Heck reaction could also operate with other types of electronically poor, acyclic alkenes. To address this question the methyl sulfone **1j**, the sulfonamide **1k**, the phosphine oxide **1l**, the phosphonate **1m**, the ester **1n**, and the phenyl ketone **1o**, all with an isopropyl group in the β-position of the alkene, were treated with PhI/$Pd(OAc)_2/Ag_2CO_3$ under the usual conditions. The results are summarized in Table 3.

Table 3. Palladium-catalyzed reaction of alkenes **1j–o** with iodobenzene.[a]



Entry	Alkene	W	**3**:**4** [%][b]	Yield[c] **4**(%)
1	**1a**	SO_2Ph	**3a**:**4a** = 5:95	86 (69)[d]
2	**1j**	SO_2Me	**3j**:**4j** = 11:89	77 (52)[d]
3	**1k**	SO_2NEt_2	**3k**:**4k** = 21:79	55
4	**1l**	$P(O)Ph_2$	**3l**:**4l** = 53:47	37
5	**1m**	PO_3Et_2	**3m**:**4m** = 65:35	24
6	**1n**	CO_2Et	**3n**:**4n** = 82:18	–[e]
7	**1o**	COPh	**3o**[f]:**4o** = 91:9	–[e]

[a] Reaction conditions: PhI (10 equiv), $Pd(OAc)_2$ (10 mol%), Ag_2CO_3 (200 mol%), DMF, 120 °C. [b] Determined by ^1H NMR spectroscopy of the crude mixtures. [c] Yield after flash chromatography. [d] Yield after flash chromatography and further recrystallization. [e] The minor compounds **4n** and **4o** could not be completely purified by chromatography or recrystallization. Significant shifts of these compounds are given in the experimental section. [f] Mixture of isomers.

Gratifyingly, the methyl sulfone **1j** (Table 3, entry 2) and the sulfonamide **1k** (Table 3, entry 3) gave similar results to that obtained from the corresponding phenyl sulfone **1a** (Table 3, entry 1). Thus, in both cases the reaction with iodobenzene occurred mainly through the domino arylation pathway (**3j**:**4j** = 11:89 and **3k**:**4k** = 21:79).

Interestingly this kind of intermolecular cascade arylation is not exclusively limited to the case of α,β-unsaturated sulfones and related sulfur compounds. As shown in entries 4 and 5 in Table 3, the α,β-unsaturated phosphine oxide **1l** and the α,β-unsaturated phosphonate **1m** gave substantial amounts of the corresponding dihydrophenanthrenes **4l** and **4m**, although the cascade/Heck selectivity was much poorer (**3l**:**4l** = 53:47; **3m**:**4m** = 65:35). After chromatographic separation of these mixtures, the Heck products **3l** and **3m** were isolated in 38 and 53% yields, respectively, whereas the products **4l** and **4m** were obtained in 37 and 24% yields, respectively.

By contrast, a very different result was observed in the arylation of typical π-conjugated, electron-deficient olefins such as the ester **1n** and the enone **1o** (entries 6-7). In these cases only minor amounts of the dihydrophenanthrenes **4** could be detected by NMR spectroscopy, and the Heck products largely predominated.

These results suggest that the relative stabilization of the C=C bond by π-conjugation with the electron-withdrawing group could be an important factor in the competition between Heck reaction and cascade arylation. Thus, in

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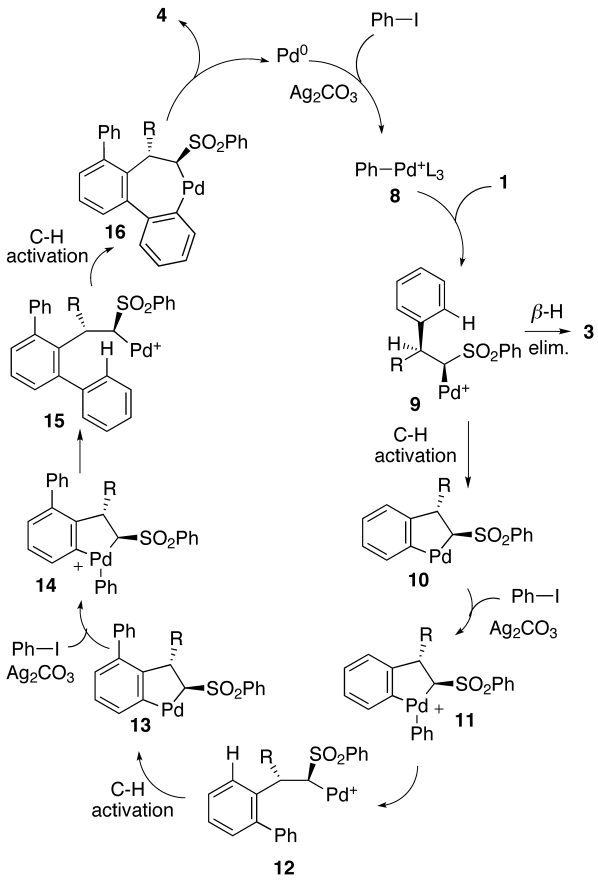
agreement with the fact that in the arylation the starting C=C bond is not regenerated, it is observed that the higher the thermodynamic stability of the C=C bond (as in the case of the π-conjugated olefins **1n** and **1o**), the lower the formation of the dihydrophenanthrene product. In other words, in the case of α,β-unsaturated sulfones, in which it is well known that the sulfonyl group does not furnish significant stability to the C=C bond,[14] the Heck reaction is less favored to such extent that the competitive domino arylation process becomes the main process.

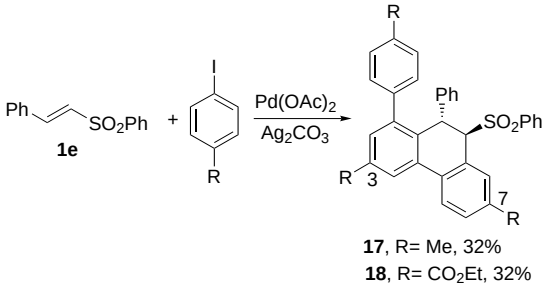
Mechanistic hypothesis: Although the complex multistep nature of this reaction makes any detailed mechanistic rationalization very difficult, a Pd^0-Pd^{II}-Pd^{IV} mechanistic pathway similar to that proposed by Catellani et al. for the cascade arylation of norbornene can be tentatively proposed[10] (Scheme 6). The oxidative addition of iodobenzene



Scheme 6. Mechanistic proposal (the ligands at the palladium center have been omitted for clarity).

to the Pd^0 catalyst in the presence of Ag_2CO_3 would give the cationic phenylpalladium species **8**. This species would undergo a regioselective *syn*-insertion to the C=C bond to generate the sulfonylalkylpalladium intermediate **9**. At this point, unlike the usual behavior of an acyclic alkene in a Heck arylation, the highly electrophilic complex **9** would evolve faster through an aromatic C–H activation process, to form the five-membered palladacycle[20] **10**, rather than by *syn*-β-hydrogen elimination to afford the minor Heck product **3**. Since reductive elimination in **10** is not expected to be a very favorable process owing to the strained nature of the resulting benzocyclobutane, palladacycle **10** could undergo oxidative addition of iodobenzene to form the Pd^{IV}[21] palladacycle species[22] **11**, which would lead to the σ-alkylpalladium intermediate **12** by a fast reductive elimination process.[23] The repetition of the same sequence of steps to the second *ortho* C–H position (palladacycle formation, oxidative addition to iodobenzene, and reductive elimination (**12**–**13**–**14**–**15**)) would furnish the next σ-sulfonylalkylpalladium species (**15**). Once both *ortho* positions of the initially inserted aromatic ring have been substituted, intermediate **15** could evolve by an aromatic C–H activation process on one of the external phenyl rings to form the seven-membered palladacycle[24] **16.** This intermediate would finally undergo a very favorable reductive elimination process (with formation of the central six-membered ring), releasing the Pd^0 catalyst and the final product **4**.

In agreement with the sequence of formation of C–C bonds depicted in Scheme 6, in the palladium-catalyzed reaction of **1e** with *para*-substituted iodoarenes, such as *p*-iodotoluene and ethyl *p*-iodobenzoate, only the dihydrophenanthrenes with substitution at the C3 and C7 positions (compounds **17** and **18**, Scheme 7) were isolated (about 32% yield after

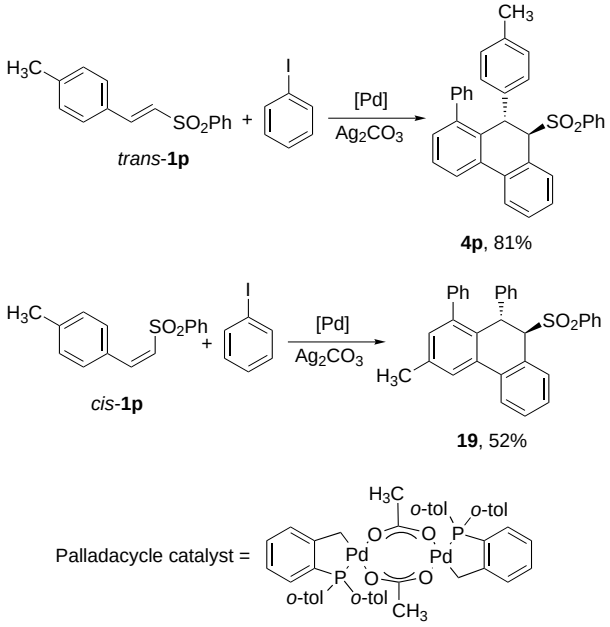


Scheme 7. Reaction of **1e** with *p*-substituted iodoarenes. Reaction conditions: ArI (10 equiv), $Pd(OAc)_2$ (10 mol%), Ag_2CO_3 (200 mol%), DMF, 120°C, 11 days.

chromatographic purification and further recrystallization from diethyl ether).[25] The structures of **17** and **18** were unequivocally established by mass spectrometry and NMR spectroscopy experiments (^{1}H NMR, ^{13}C NMR, COSY, and NOESY)[26].

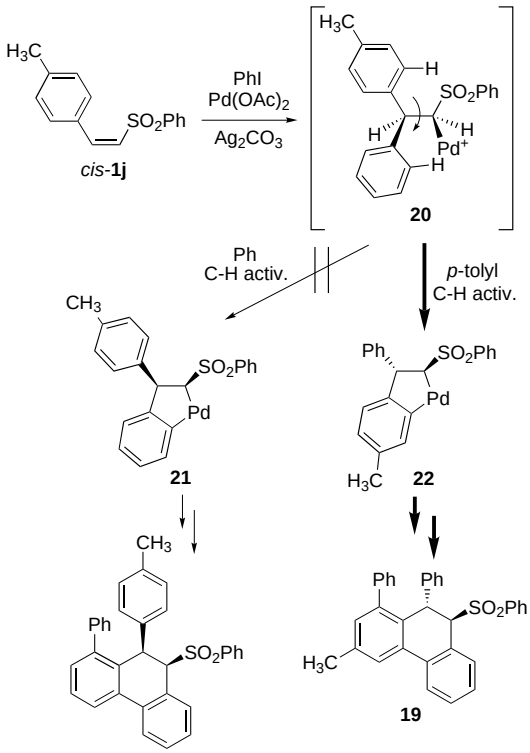
Reaction of *cis*-substituted α,β-unsaturated sulfones: From a stereochemical point of view, the exclusive formation of C9/C10 *trans*-substituted dihydrophenanthrenes from *trans*-α,β-unsaturated sulfones would indicate that the configuration of the starting alkene is preserved along the reaction course, which is consistent with an initial *syn*-carbopalladation step and further aromatic C–H activation processes through the participation of *trans*-substituted palladacycles as indicated in Scheme 6. This high stereoselectivity prompted us to investigate the behavior of a *cis*-substituted α,β-unsaturated sulfone, since if a parallel diastereomeric pathway occurred, C9/C10 *cis*-substituted dihydrophenanthrenes could be obtained.

To properly compare the outcome of the reaction, the pair of diastereomeric phenyl sulfones *trans*-**1p** and *cis*-**1p**, with a "methyl-labeled" substituent in the β-position (a *p*-tolyl group), were stereoselectively prepared according to reported procedures[13][27] and treated with iodobenzene/Ag_2CO_3 in the presence of a palladium catalyst. In these cases we observed that the cascade:Heck product ratio was very high when we used a palladacycle catalyst[28] instead of $Pd(OAc)_2$ (Scheme 8). *trans*-**1p** behaved as expected, affording the C9/C10 *trans*-substituted dihydrophenanthrene **4p** (81% yield),



Scheme 8. Palladium-catalyzed reaction of *trans*-**1p** and *cis*-**1p** with iodobenzene. Reaction conditions: PhI (10 equiv), palladacycle catalyst (5 mol%), Ag_2CO_3 (200 mol%), DMF, 120 °C.

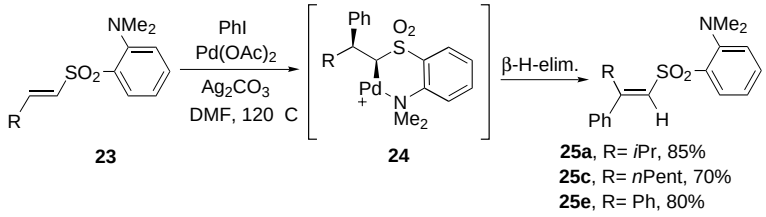
in which the starting *p*-tolyl group is bound to the C10 position. Unexpectedly, the reaction of *cis*-**1p** also led to the major formation of a single dihydrophenantrene with *trans* stereochemistry at C9/C10, but with the methyl group of the starting *p*-tolyl moiety in position C3 of the final dihydrophenanthrene (compound **19**, 52% yield).[29] The seemingly anomalous formation of **19** could be readily explained by taking into account that, once the *syn* carbopalladation step occurred, the resulting σ-alkylpalladium intermediate **20** would undergo a C–H activation process at the *p*-tolyl moiety, and not at the phenyl group introduced after the *syn* carbopalladation step, in order to avoid the formation of the *cis*-substituted palladacycle **21**, which is presumably less stable than the corresponding *trans* analogue **22** (Scheme 9).



Scheme 9. Mechanistic proposal for the reaction of *cis*-**1p**.

Reaction of α,β-unsaturated 2-(*N*,*N*-dimethylamino)phenyl sulfones: In our previous studies on Heck reactions of α,β-unsaturated aryl sulfoxides with PhI/Ag_2CO_3 the use of the 2-(*N*,*N*-dimethylamino)phenyl moiety as a substituent on the sulfur proved to be critical to the success of this reaction.[5] Compared to the sluggish reaction observed from the corresponding phenyl sulfoxides, we justified the high reactivity of the 2-(*N*,*N*-dimethylamino)phenyl sulfoxides as a result of the pseudointramolecular character of the reaction because of the coordination of the palladium atom to the *N*,*N*-dimethylamino group (Pd–N chelation-controlled reaction). These findings prompted us to investigate the behavior of the corresponding α,β-unsaturated 2-(*N*,*N*-dimethylamino)phenyl sulfones **23** under the standard arylation conditions [PhI, Ag_2CO_3, $Pd(OAc)_2$].

Interestingly, the α,β-unsaturated sulfones **23** behaved as expected for an acyclic alkene under Heck reaction conditions, affording in each case the corresponding trisubstituted olefin **25**[30] in high yield and with complete *E* stereoselectivity (70–85% yield, Scheme 10). The corresponding dihydrophenanthrene was not detected by ^1H NMR spectroscopy even in the presence of the usual large excess of iodobenzene. This opposite result to that described from sulfones **1** is in agreement with our assumption that the cascade arylation of α,β-unsaturated phenyl sulfones requires the participation of



Scheme 10. Heck reaction of α,β-unsaturated sulfones **23** with iodobenzene.

highly electrophilic σ-alkylpalladium species in order to promote the key *ortho* C–H activation steps. Thus, in the case of olefins **23** the insertion of the arylpalladium species into the C=C bond would presumably lead to the Pd–N chelated σ-alkylpalladium intermediate **24**, which would undergo a *syn* β-hydrogen elimination process, and not a C–H activation process, as a result of the diminished electrophilic character of the palladium atom caused by its coordination with the highly donating nitrogen atom. It should also be noted that conceptually similar Pd–N chelation controlled Heck reactions have been described for other types of alkenes bearing chains with an appropriately located nitrogen atom.[31]

Conclusion

Compared to any other type of acyclic 1,2-disubstituted alkene, β-substituted α,β-unsaturated phenyl sulfones display unique behavior under arylation Heck conditions. In the presence of Ag_2CO_3 as base, their palladium-catalyzed reactions ($Pd(OAc)_2$ as catalyst, in DMF at 120 °C) with iodobenzene (or *p*-substituted iodoarenes) occurred mainly by a cascade process (involving one molecule of vinyl sulfone and three molecules of iodobenzene) rather than by a normal Heck arylation, affording *trans*-9-(phenylsulfonyl)-9,10-dihydrophenanthrenes (compounds **4**). This result indicates that, unlike the usual behavior of an alkene under Heck reaction conditions, the σ-alkylpalladium intermediate formed after the starting insertion step can evolve faster by successive *ortho* C–H activation steps, with consequent formation of five-membered palladacycle intermediates, than by a β-hydrogen elimination process.

Although not so favorable as in the case of α,β-unsaturated sulfones, such cascade arylation also occurs with related electronically poor olefins like α,β-unsaturated sulfonamides, phosphine oxides, and α,β-unsaturated phosphonates. In contrast, typical π-conjugated olefins such as α,β-unsaturated esters and enones almost exclusively afforded the Heck-type products.

Experimental Section

General: Chemical shifts in NMR spectra are expressed in ppm. All NMR spectra were obtained in $CDCl_3$ at room temperature. Both chemical shifts and coupling constants (Hz) were obtained by first order analysis of spin patterns. High resolution mass spectra were recorded by using FAB technique. Analitycal thin layer chromatography was performed on DC-Alufolien 0.2 mm silica gel 60 F_{254} (MERCK). Visualization was accomplished with UV light and ethanolic phosphomolybdic acid solution followed by heating. Flash chromatography was performed on silica gel MERCK-60 (230–400 mesh). All reagents were obtained from commercial suppliers and were used without further purification except for aldehydes, which were used freshly distilled. DMF was distilled from CaH_2. THF was distilled from sodium/benzophenone. CH_2Cl_2 was distilled from P_2O_5. All reactions involving the use of *n*BuLi or $Pd(OAc)_2$ were carried out in flame and oven dried glassware under inert argon atmosphere.

General procedure for the preparation of dihydrophenanthrenes (4, 17, 18, and 19) and characterization data of the main products: A mixture of the corresponding alkene **1** (0.4 mmol), silver carbonate (0.8 mmol, 200 mol %), $Pd(OAc)_2$ (0.04 mmol, 10 mol %), aryl iodide (4 mmol, 1000 mol %), and DMF (2 mL) was heated at 120 °C under vigorous stirring and argon atmosphere. When the starting alkene disappeared by TLC (3–11 days, the particular reaction time is indicated below for each case) the mixture was allowed to cool to room temperature and was diluted with Et_2O (20 mL), filtered through celite, washed with water (20 mL), dried ($MgSO_4$), and evaporated. The residue was purified by flash chromatography (the eluent is indicated below for each case). Where indicated, pure samples of dihydrophenanthrenes were obtained by further recrystallization from Et_2O.

10-Isopropyl-1-phenyl-9-(phenylsulfonyl)-9,10-dihydrophenanthrene (4a): Reaction time three days. Eluent hexane/diethyl ether (10:1), 86 % yield. Recrystallization from diethyl ether, 69 % overall yield. M.p. 182–184 °C; ^{1}H NMR (200 MHz): $\delta = 7.71-7.68$ (m, 2H), 7.59–7.23 (m, 8H), 7.16–6.93 (m, 7H), 4.54 (d, $J = 1.9$ Hz, 1H), 4.07 (dd, $J = 1.9$ and 7.5 Hz, 1H), 1.35 (m, 1H), 0.53 (d, $J = 6.7$ Hz, 3H), 0.44 ppm (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (75 MHz): $\delta = 142.5$, 141.3, 136.4, 135.9, 132.9, 132.7, 131.3, 130.7, 129.8, 128.9, 128.3, 127.9, 127.6, 127.1, 127.0, 123.8, 123.0, 69.0, 40.2, 32.3, 20.8, 19.5 ppm; MS (FAB +): (*m*/*z*): 461 $[M + Na]^+$, 297 $[M - PhSO_2]^+$, 255, 154, 95; elemental analysis calcd (%) for $C_{29}H_{26}O_2S$: C 79.42, H 5.98, S 7.31; found: C 79.22, H 5.81, S 6.85. Crystal structure data for $C_{29}H_{26}O_2S$ (**4a**): crystal size $0.20 \times 0.35 \times 0.25$ mm, monoclinic, space group $P2_1/c$, $a = 13.3746(6)$, $b = 8.8535(5)$, $c = 20.5133(9)$ Å, $\beta = 106.860(4)^0$, $V = 2324.6(2)$ Å^3, $Z = 5$, $\rho_{calcd} = 1.566$ Mg m^{-3}, $\mu = 1.764$ mm^{-1}, $2\theta_{max} = 113.94^0$, $Cu_{K\alpha}$ radiation, $\lambda = 1.54178$ Å, $2\theta/\omega$ scans, $T = 296$ K, absorption correction: none, 4119 reflections collected, 3076 independent. Refinement on F^2 for 3076 reflections and 524 parameters gave GOF = 1.053, $R1 = 0.0322$ and $wR2 = 0.0853$ for $I > 2\sigma(I)$. Residual electron density $-0.313 < \Delta\rho < 0.220$ eÅ^{-3}. S, O, and C atoms were refined with anisotropic thermal displacements parameters and the H atoms with isotropic parameters. The structure was solved and refined using SHELX-97.[32]

10-*n*-Pentyl-1-phenyl-9-(phenylsulfonyl)-9,10-dihydrophenanthrene (4c): Reaction time three days. Eluent hexane/diethyl ether (10:1), 82 % yield: (**3c**:**4c** = 12:88; **4c** was partially separated by chromatography). ^{1}H NMR (300 MHz): $\delta = 7.60-7.27$ (m, 10H), 7.18–6.96 (m, 7H), 4.35 (d, $J = 1.6$ Hz, 1H), 4.11 (ddd, $J = 1.6$, 5.0, and 9.3 Hz, 1H), 1.30–0.66 ppm (m, 11H); ^{13}C NMR (75 MHz): $\delta = 154.5$, 153.7, 149.5, 148.4, 147.3, 145.7, 145.1, 145.0, 143.4, 142.8, 142.4, 142.0, 141.3, 141.2, 140.9, 140.6, 140.3, 140.2, 139.8, 139.2, 136.9, 136, 82.8, 47.4, 46.5, 43.6, 38.9, 35.1, 26.8 ppm; HRMS (FAB +): calcd for $C_{25}H_{25}$ ($[M - PhSO_2]^+$) 325.1956, found 325.1960.

10-Cyclohexyl-1-phenyl-9-(phenylsulfonyl)-9,10-dihydrophenanthrene (4d): Reaction time four days. Eluent hexane/diethyl ether (10:1), 84 % yield: (**3d**:**4d** = 10:90; **4d** was partially separated by chromatography). ^{1}H NMR (300 MHz): $\delta = 7.70-7.68$ (m, 2H), 7.62–7.25 (m, 8H), 7.14–6.96 (m, 7H), 4.51 (d, $J = 1.6$ Hz, 1H), 4.10 (dd, $J = 1.7$ and 7.1 Hz, 1H), 1.5–0.4 ppm (m, 11H); ^{13}C NMR (75 MHz): $\delta = 142.5$, 141.3, 136.5, 136.0, 133.0, 132.6, 132.5, 131.4, 130.7, 129.8, 129.7, 128.9, 128.7, 128.3, 127.9, 127.6, 127.2, 127.0, 123.8, 122.9, 68.9, 42.1, 39.5, 30.9, 29.7, 26.3, 26.2, 25.9 ppm; HRMS (FAB +): calcd for $C_{26}H_{25}$ ($[M - PhSO_2]^+$) 337.1956, found 337.1964.

1,10-Diphenyl-9-(phenylsulfonyl)-9,10-dihydrophenanthrene (4e): Reaction time five days. Eluent hexane/diethyl ether (10:1), 82 % yield. Recrystallization from diethyl ether, 63 % yield. M.p. 155–157 °C; ^{1}H NMR (300 MHz): $\delta = 7.70-7.66$ (m, 1H), 7.45–7.01 (m, 19H), 6.72–6.87 (m, 2H), 5.06 (d, $J = 1.1$ Hz, 1H), 4.4 ppm (d, $J = 1.1$ Hz, 1H); ^{13}C NMR (75 MHz): $\delta = 142.7$, 141.4, 140.3, 136.1, 135.9, 133.7, 132.9, 132.4, 131.2, 130.3, 130.0, 129.0, 128.5, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4, 126.7, 125.4, 123.7, 123.1, 73.3, 41.6 ppm; HRMS (FAB +): calcd for $C_{32}H_{25}O_2S$ ($[M + H]^+$) 473.1575, found 473.1564. Crystal structure data for $C_{32}H_{24}O_2S$ (**4e**): crystal size $0.07 \times 0.4 \times 0.2$ mm, triclinic, space group $P\bar{1}$, $a = 9.5089(14)$, $b = 10.0130(11)$, $c = 13.1809(12)$ Å, $\alpha = 74.739(8)$, $\beta = 83.950(9)$, $\gamma = 79.955(10)^0$, $V = 1189.8(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.319$ Mg m^{-3}, $\mu = 1.424$ mm^{-1}, $2\theta_{max} = 114.5^0$, $Cu_{K\alpha}$ radiation, $\lambda = 1.54178$ Å, $2\theta/\omega$ scans, $T = 296$ K, absorption correction: empirical (min./max. transmission: 0.3332/0.4135). 3795 reflections collected, 3138 independent. Refinement on F^2 for 3138 reflections and 533 parameters gave GOF = 1.024, $R1 = 0.0318$ and $wR2 = 0.0863$ for $I > 2\sigma(I)$. Residual electron density $-0.218 < \Delta\rho < 0.145$ eÅ^{-3}. S, O, and C atoms were refined with anisotropic thermal displacements parameters and the H atoms with isotropic parameters. The structure was solved and refined using SHELX-97.[32]

10-β-Naphthyl-1-phenyl-9-(phenylsulfonyl)-9,10-dihydrophenanthrene (4f): Reaction time five days. Eluent hexane/diethyl ether (10:1), 85 % yield. Recrystallization from diethyl ether, 61 % yield. M.p. 158–160 °C;

^{1}H NMR (300 MHz): $\delta = 8.10-6.90$ (m, 24H), 5.28 (d, $J = 1.4$ Hz, 1H), 4.53 ppm (d, $J = 1.4$ Hz, 1H); ^{13}C NMR (75 MHz): $\delta = 142.7$, 142.5, 140.2, 138.8, 137.7, 136.0, 135.9, 133.8, 133.3, 133.2, 132.9, 132.7, 132.3, 132.2, 130.9, 130.8, 130.3, 130.0, 129.3, 128.9, 128.4, 127.8, 127.4, 126.9, 125.8, 125.7, 125.6, 125.4, 123.7, 123.2, 73.2, 41.7 ppm; HRMS (FAB+): calcd for $C_{30}H_{21}$ ($[M-PhSO_2]^+$) 381.1643, found 381.1624.

10-(2,2-Diphenylethenyl)-1-phenyl-9-(phenylsulfonyl)-9,10-dihydrophenanthrene (4h): Reaction time five days. Eluent hexane/diethyl ether (10:1), 57% yield from **1h**, 58% from **1i**. Recrystallization from diethyl ether, 47% yield from **1h**, 48% from **1i**. ^{1}H NMR (300 MHz): $\delta = 7.68$ (m, 1H), 7.49–7.21 (m, 13H), 7.18–6.96 (m, 9H), 6.86 (m, 2H), 6.66 (m, 2H), 5.46 (d, $J = 9.1$ Hz, 1H), 4.95 (dd, $J = 1.8$ and 9.1 Hz, 1H), 4.36 ppm (d, $J = 1.8$ Hz, 1H); ^{13}C NMR (125 MHz): $\delta = 149.4$, 143.8, 142.6, 142.3, 140.9, 138.6, 137.1, 136.1, 133.1, 133.0, 132.8, 132.3, 131.0, 130.4, 129.6, 129.5, 129.3, 128.9, 128.8, 128.5, 128.3, 128.2, 127.8, 127.7, 127.5, 126.7, 124.5, 123.8, 71.4, 36.3, 15.7 ppm; HRMS (FAB+): calcd for $C_{34}H_{25}$ ($[M-PhSO_2]^+$) 433.1956, found 433.1963. Crystal structure data for $C_{40}H_{30}O_2S$ (**4h**): crystal size $0.15 \times 0.25 \times 0.20$ mm, monoclinic, space group $P2_1$, $a = 8.62810(10)$, $b = 14.1813(2)$, $c = 12.91000(10)$ Å, $\beta = 108.9390(10)^0$, $V = 1494.12(3)$Å^3, $Z = 2$, $\rho_{calcd} = 1.277$ Mg m^{-3}, $\mu = 1.231$ mm^{-1}, $2\theta_{max} = 141.02^0$, $Cu_{K\alpha}$ radiation, $\lambda = 1.54178$ Å, $2\theta/\omega$ scans, $T = 296$ K, absorption correction: SADABS versus 2.03, 2797 reflections collected. Refinement on F^2 for 2797 reflections, 389 parameters and one restraint gave GOF = 1.044, $R1 = 0.0288$, and $wR2 = 0.0819$ for $I > 2\sigma(I)$. Residual electron density $-0.161 < \Delta\rho < 0.186$ eÅ^{-3}. S, O, and C atoms were refined with anisotropic thermal displacements parameters and the H atoms with isotropic parameters. The structure was solved and refined using SHELX-97.[32]

1-Phenyl-9-(methylsulfonyl)-10-isopropyl-9,10-dihydrophenanthrene (4j): Reaction time 3.5 days. Eluent hexane/diethylether (8:1), 77% yield. Recrystallization from diethylether, 52% yield. M.p. 167–171 ^{0}C; ^{1}H NMR (300 MHz): $\delta = 7.92$ (d, $J = 8.1$ Hz, 1H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.57–7.36 (m, 9H), 7.25 (dd, $J = 1.2$ and 7.7 Hz, 1H), 4.26 (s, 1H), 3.93 (d, $J = 7.3$ Hz, 1H), 2.17 (s, 3H), 1.54–1.42 (m, 1H), 0.55 (d, $J = 6.9$ Hz, 3H), 0.49 ppm (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz): $\delta = 144.3$, 141.8, 136.0, 134.4, 134.1, 132.9, 132.3, 131.1, 130.7, 129.6, 129.3, 128.8, 128.1, 125.2, 124.5, 68.7, 41.4, 38.5, 33.3, 21.9, 20.5 ppm; HRMS (EI+): calcd for $C_{24}H_{24}O_2S$ ($[M^+]$) 376.1497, found 376.1479.

1-Phenyl-9-(*N*,*N*-diethylsulfamoyl)-10-isopropyl-9,10-dihydrophenanthrene (4k): Reaction time nine days. Eluent hexane/diethyl ether (8:1), 70% yield. Recrystallization from diethyl ether, 55% yield. M.p. 162–166 ^{0}C; ^{1}H NMR (300 MHz): $\delta = 7.89$ (brd, $J = 7.7$ Hz, 1H), 7.81 (brd, $J = 7.7$ Hz, 1H), 7.63–7.53 (m, 1H), 7.49–7.28 (m, 7H), 7.21–7.18 (m, 1H), 4.41 (d, $J = 1.6$ Hz , 1H), 3.88 (dd, $J = 7.7$ and 1.6 Hz, 1H), 2.86–2.55 (m, 4H), 1.49–1.37 (m, 1H), 0.93 (t, $J = 7.1$ Hz , 6H), 0.51 (d, $J = 6.9$ Hz, 3H), 0.48 ppm (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz): $\delta = 143.5$, 142.2, 136.7, 135.2, 133.8, 131.8, 131.6, 130.5, 130.1, 128.9, 128.7, 128.3, 127.7, 127.6, 124.9, 123.7, 66.2, 43.4, 41.6, 32.9, 21.7, 20.2, 15.8 ppm; HRMS (EI+): calcd for $C_{27}H_{31}NO_2S$ ($[M^+]$) 433.2076, found 433.2055.

9-(Diphenylphosphoryl)-10-isopropyl-1-phenyl-9,10-dihydrophenanthrene (4l): Reaction time five days. Eluent hexane/ethyl acetate (1:1), 37% yield. ^{1}H NMR (300 MHz): $\delta = 7.87-7.79$ (m, 2H), 7.62–7.58 (m, 1H), 7.57–7.53 (m, 1H), 7.51–7.44 (m, 2H), 7.41–7.35 (m, 2H), 7.34–7.19 (m, 5H), 7.10–6.97 (m, 8H), 6.80–6.75 (m, 1H), 4.21 (dd, $J = 1.4$ and 17.6 Hz, 1H), 3.91–3.85 (m, 1H), 1.48–1.34 (m, 1H), 0.68 (d, $J = 6.8$ Hz, 3H), 0.39 ppm (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (75 MHz) (splitting of signals due to coupling with the phosphorus atom): $\delta = 142.2$, 141.9, 137.0, 136.9, 134.4, 134.3, 133.9, 133.5, 132.2, 131.9, 131.8, 131.7, 131.6, 131.5, 131.4, 130.9, 130.8, 130.3, 130.2, 130.1, 130.0, 129.9, 129.8, 129.5, 129.3, 128.5, 128.4, 128.0, 127.9, 127.8, 127.3, 127.2, 127.1, 127.0, 126.8, 126.5, 124.3, 124.2, 123.0, 44.2, 43.3, 39.6, 39.5, 32.2, 32.0, 21.0, 20.1 ppm; HRMS (FAB+): calcd for $C_{35}H_{32}OP$ ($[M+H]^+$) 499.2191, found 499.2198.

10-Isopropyl-9-(diethoxyphosphoryl)-1-phenyl-9,10-dihydrophenanthrene (4m): Reaction time five days. Eluent hexane/ethyl acetate (1:1), 24% yield. ^{1}H NMR (300 MHz): $\delta = 7.81$ (brd, $J = 7.9$ Hz, 1H), 7.75 (brd, $J = 7.9$ Hz, 1H), 7.64 (brs, 1H), 7.49–7.41 (brt, $J = 7.4$ Hz, 2H), 7.40–7.23 (m, 6H), 7.22–7.16 (m, 1H), 3.91–3.74 (m, 3H), 3.62–3.49 (m, 2H), 3.40 (ddq, $J = 7.1$, 8.3, and 10.1 Hz, 1H), 1.48–1.33 (m, 1H), 1.10 (t, $J = 7.1$ Hz, 3H), 0.99 (t, $J = 7.1$ Hz, 3H), 0.59 (t, $J = 6.8$ Hz, 3H), 0.39 ppm (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (75 MHz) (splitting of signals due to the coupling with the phosphorus atom): $\delta = 142.7$, 141.9, 135.5, 135.5, 135.4, 135.3, 134.1, 134.0, 130.6, 130.5, 130.4, 130.3, 130.1, 128.0, 127.9, 127.8, 127.7, 127.6, 126.8, 126.7, 126.6, 123.9, 123.8, 123.2, 61.8, 61.7, 61.6, 61.5, 41.7, 40.1, 40.0, 39.9, 31.7, 31.5, 21.0, 20.0, 16.2, 16.1, 16.0 ppm; HRMS (FAB+): calcd for $C_{27}H_{32}O_3P$ ($[M+H]^+$) 435.2089, found 435.2074.

Significant ^{1}H NMR data of compound (4n): ^{1}H NMR (200 MHz): $\delta = 3.91$ (brs, 1H; H_9), 3.50 (brd, $J = 9.1$ Hz, 1H; H_{10}), 0.65 (d, $J = 6.5$ Hz, 3H; CH_3), 0.42 ppm (d, $J = 6.5$ Hz, 3H; CH_3).

Significant ^{1}H NMR data of compound (4o): ^{1}H NMR (300 MHz): $\delta = 4.92$ (d, $J = 1.6$ Hz, 1H; H_9), 3.38 (dd, $J = 1.6$ and 9.3 Hz, 1H; H_{10}), 0.87 (d, $J = 6.9$ Hz, 3H; CH_3), 0.45 ppm (d, $J = 6.9$ Hz, 3H; CH_3).

1-Phenyl-9-(phenylsulfonyl)-10-(*p*-tolyl)-9,10-dihydrophenanthrene (4p): Reaction time five days (a palladacycle catalyst[28] was used instead of $Pd(OAc)_2$). Eluent hexane/diethyl ether (10:1), 81% yield. ^{1}H NMR (300 MHz): $\delta = 7.68$ (d, $J = 7.3$ Hz, 1H), 7.41 (dt, $J = 1.8$ and 7.1 Hz, 1H), 7.36–7.22 (m, 8H), 7.21–7.11 (m, 2H), 7.10–7.00 (m, 5H), 6.85 (d, $J = 8.1$ Hz, 2H), 6.59 (d, $J = 8.1$ Hz, 2H), 5.03 (brs, 1H), 4.39 (d, $J = 1.2$ Hz, 1H), 2.19 ppm (s, 3H); ^{13}C NMR (75 MHz): $\delta = 142.6$, 140.3, 138.4, 136.2, 136.1, 136.0, 135.9, 133.6, 132.9, 132.4, 131.3, 130.4, 129.9, 129.2, 129.0, 128.9, 128.0, 127.7, 127.6, 127.5, 127.3, 125.5, 123.7, 123.0, 73.4, 41.1, 20.9 ppm; HRMS (FAB+): calcd for $C_{27}H_{21}$ ($[M-PhSO_2]^+$) 345.1643, found 345.1635.

3,7-Dimethyl-10-phenyl-9-(phenylsulfonyl)-1-(*p*-tolyl)-9,10-dihydrophenanthrene (17): Reaction time 11 days. Eluent hexane/diethyl ether (8:1), 69% Yield. Recrystallization from diethyl ether, yield: 32%. M.p. 210–212 ^{0}C; ^{1}H NMR (500 MHz): $\delta = 7.53$ (d, $J = 8.1$ Hz, 1H), 7.35–7.30 (m, 1H), 7.20 (dd, $J = 1.8$ and 8.1 Hz, 1H), 7.10–7.02 (m, 11H), 6.96 (brs, 1H), 6.92 (brs, 1H), 6.93–6.87 (m, 1H), 6.77–6.74 (m, 2H), 5.00 (brs, 1H), 4.34 (d, $J = 1.3$ Hz, 1H), 2.38 (s, 3H), 2.30 (s, 3H), 2.27 ppm (s, 3H); ^{13}C NMR (75 MHz): $\delta = 143.1$, 142.5, 138.4, 138.2, 137.5, 136.7, 134.5, 134.2, 133.5, 132.9, 131.5, 129.7, 129.5, 129.3, 129.1, 128.6, 128.5, 128.3, 128.2, 128.1, 127.2, 126.1, 124.2, 124.2, 74.4, 42.1, 21.9, 21.8, 21.7 ppm; HRMS (FAB+): calcd for $C_{29}H_{25}$ ($[M-PhSO_2]^+$) 373.1956, found 373.1941.

3,7-(Diethoxycarbonyl)-1-[4-(ethoxycarbonyl)phenyl]-10-phenyl-9-(phenylsulfonyl)-9,10-dihydrophenanthrene (18): Reaction time 11 days. Eluent hexane/diethyl ether (8:1), 69% yield. Recrystallization from diethyl ether, 32% yield. M.p. 155–156 ^{0}C; ^{1}H NMR (500 MHz): $\delta = 8.19$ (brs, 1H), 8.15 (brd, $J = 8.4$ Hz, 1H), 8.02 (d, $J = 7.6$ Hz, 2H), 7.95 (brd, $J = 8.4$ Hz, 1H), 7.88 (brs, 1H), 7.76 (brs, 1H), 7.45–7.39 (m, 1H), 7.20–7.05 (m, 9H), 6.67–6.62 (m, 2H), 5.10 (brs, 1H), 4.47 (brs, 1H), 4.50–4.39 (m, 4H), 4.35 (q, $J = 7.2$ Hz, 2H), 1.45 (t, $J = 7.2$ Hz, 3H), 1.44 (t, $J = 7.1$ Hz, 3H), 1.38 ppm (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz): $\delta = 167.0$, 166.4, 166.2, 144.4, 142.8, 140.5, 139.7, 137.3, 136.4, 134.2, 134.1, 134.0, 132.2, 132.0, 131.0, 130.8, 130.7, 130.1, 129.7, 129.7, 129.6, 128.9, 128.3, 128.0, 126.4, 125.8, 125.0, 73.2, 62.1, 62.0, 61.8, 42.1, 15.1, 15.0, 14.9 ppm; HRMS (FAB+): calcd for $C_{35}H_{31}O_6$ ($[M-PhSO_2]^+$) 547.2120, found 547.2105.

3-Methyl-1,10-diphenyl-9-(phenylsulfonyl)-9,10-dihydrophenanthrene (19): Reaction time five days (a palladacycle catalyst was used instead of $Pd(OAc)_2$)[28]. Eluent hexane/diethyl ether (10:1), 52% yield. ^{1}H NMR (500 MHz): $\delta = 7.65$ (brd, $J = 7.9$ Hz, 1H), 7.38 (dt, $J = 2.0$ and 6.9 Hz, 1H), 7.36–7.32 (m, 1H), 7.31–7.27 (m, 5H), 7.22 (dt, $J = 0.9$ and 7.3 Hz, 1H), 7.09–7.02 (m, 9H), 6.95 (brs, 1H), 6.73–6.68 (m, 2H), 5.00 (s, 1H), 4.38 (s, 1H), 2.30 ppm (s, 3H); ^{13}C NMR (75 MHz): $\delta = 142.5$, 141.5, 140.4, 137.0, 136.1, 136.0, 133.7, 132.3, 131.1, 129.9, 129.0, 128.9, 128.5, 128.2, 128.0, 127.9, 127.8, 127.7, 127.3, 126.6, 125.6, 123.9, 123.7, 73.6, 41.3, 21.1 ppm; HRMS (FAB+): calcd for $C_{27}H_{21}$ ($[M-PhSO_2]^+$) 345.1643, found 345.1634.

Diphenyl [(*E*)-3-methyl-2-phenyl-1-butenyl]phosphine oxide (3l) b: Reaction time five days. Eluent hexane/ethyl acetate (1:1), yield 38%. ^{1}H NMR (300 MHz): $\delta = 7.82-7.74$ (m, 4H), 7.52–7.38 (m, 6H), 7.34–7.27 (m, 3H), 7.23–7.18 (m, 2H), 5.94 (m, $J = 25.7$ Hz, 1H), 3.79 (m, 1H), 0.95 ppm (d, $J = 6.87$ Hz, 6H); ^{13}C NMR (75 MHz) (splitting of signals due to coupling with the phosphorus atom): $\delta = 171.6$, 171.5, 141.1, 140.9, 135.6, 134.2, 131.5, 131.4, 130.9, 130.8, 128.6, 128.4, 128.3, 128.2, 127.7, 127.6, 127.5, 127.2, 127.1, 127.0, 121.0, 119.6, 32.7, 32.6, 21.0 ppm; HRMS (FAB+): calcd for $C_{23}H_{24}OP$ ($[M+H]^+$) 347.1565, found 347.1563.

Diethyl [(*E*)-3-methyl-2-phenyl-1-butenyl] phosphonate (3m): Reaction time five days. Eluent, hexane/ethyl acetate (1:1), yield 53%. ^{1}H NMR (300 MHz): $\delta = 7.35-7.29$ (m, 3H), 7.19–7.15 (m, 2H), 5.43 (d, $J = 18.8$ Hz, 1H), 4.12 (m, 4H), 3.80–3.68 (m, 1H), 1.35 (t, $J = 7.1$ Hz, 6H), 1.08 ppm (d, $J = 6.87$ Hz, 6H); ^{13}C NMR (75 MHz) (splitting of signals due to coupling with the phosphorus atom): $\delta = 170.6$, 170.4, 141.0, 140.6, 127.7, 127.6, 127.6,

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116.5, 114.1, 61.5, 61.4, 32.5, 32.4, 21.3, 16.4, 16.3 ppm; HRMS (FAB+): calcd for $C_{15}H_{24}O_3P$ ([M^+]) 283.1463, found 283.1473.

(*E*)-1,2-Diphenyl-3-methyl-3-pentenone (3o) (isolated as major isomer in a mixture of isomers): Reaction time: 1.5 days. Eluent hexane/dichloromethane (1:1), 71% yield. ^{1}H NMR (300 MHz): $\delta = 7.69-7.61$ (m, 2H), 7.46–7.27 (m, 8H), 6.06 (s, 1H), 3.00 (s, 1H), 1.74 (s, 3H), 1.61 ppm (s, 3H); ^{13}C NMR (75 MHz): $\delta = 149.8$, 143.1, 133.0, 128.5, 128.3, 128.1, 127.3, 126.6, 125.8, 107.2, 88.9, 29.8, 27.5 ppm.

General procedure for the preparation of dihydrophenanthrenes 7: Under an argon atmosphere, recently prepared, finely divided Na–Hg (6%, 200 mg) was added to a solution of dihydrophenanthrene **4** (1 mmol) in a THF/MeOH (1:1) mixture (1 mL). After the mixture had been stirred at room temperature for 12 h, another portion of Na–Hg (100 mg) was added to bring the reaction to completion. The reaction mixture was then washed with NaOH (2M, 3 mL), the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. The residue was purified by flash chromatography to give the corresponding dihydrophenanthrene **7** (the eluent and yield are indicated below for each case).

10-Isopropyl-1-phenyl-9,10-dihydrophenanthrene (7a) b: Reaction time 24 h. Eluent hexane/diethyl ether (4:1), 99% yield. M.p. 106–107 °C; ^{1}H NMR (300 MHz): $\delta = 7.81$ (t, $J = 7.4$ Hz, 2H), 7.51–7.11 (m, 10H), 3.19–2.90 (m, 3H), 1.49–1.25 (m, 1H), 0.64 (d, $J = 6.7$ Hz, 3H), 0.39 ppm (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (75 MHz): $\delta = 142.3$, 142.2, 138.7, 135.5, 135.2, 134.2, 129.9, 129.4, 128.5, 127.9, 127.5, 126.7, 126.5, 126.2, 123.5, 123.4, 40.2, 32.1, 29.7, 21.4, 20.4 ppm; HRMS (FAB+): calcd for $C_{23}H_{22}$ ([M^+]) 298.1721, found 298.1733.

1,10-Diphenyl-9,10-dihydrophenanthrene (7e): Reaction time 24 h. Eluent hexane/diethyl ether (4:1), 99% yield. M.p. 154–155 °C; ^{1}H NMR (300 MHz): $\delta = 7.94$ (dd, $J = 1.0$ and 8.0 Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 2H), 7.37–6.96 (m, 12H), 6.83–6.78 (m, 2H), 4.25 (dd, $J = 2.0$ and 6.0 Hz, 1H), 3.35 (dd, $J = 6.0$ and 15.0 Hz, 1H), 2.96 ppm (dd, $J = 2.0$ and 15.0 Hz, 1H); ^{13}C NMR (75 MHz): $\delta = 141.0$, 136.0, 135.3, 135.0, 134.3, 129.7, 129.2, 128.8, 128.3, 127.9, 127.8, 127.7, 127.3, 127.1, 126.9, 125.7, 123.6, 40.5, 37.5 ppm; HRMS (FAB+): calcd for $C_{26}H_{20}$ (M^+) 332.1565, found 332.1559.

10-β-Naphthyl-1-phenyl-9,10-dihydrophenanthrene (7f): Reaction time 24 h. Eluent hexane/diethyl ether (4:1), 96% yield. M.p. 130–131 °C; ^{1}H NMR (300 MHz): $\delta = 7.94$ (dd, $J = 1.0$ and 8.0 Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 2H), 7.37–6.96 (m, 12H), 6.83–6.78 (m, 2H), 4.43 (dd, $J = 1.6$ and 5.8 Hz, 1H), 3.43 (dd, $J = 5.8$ and 15.0 Hz, 1H), 3.06 ppm (dd, $J = 1.6$ and 15.0 Hz, 1H); ^{13}C NMR (75 MHz): $\delta = 142.2$, 141.4, 141.2, 135.9, 135.5, 135.1, 134.3, 133.3, 131.9, 129.8, 129.2, 128.8, 127.8, 127.7, 127.6, 127.4, 127.3, 127.1, 127.0, 126.6, 126.5, 125.5, 125.1, 123.8, 123.6, 40.7, 37.4 ppm; HRMS (FAB+): calcd for $C_{30}H_{22}$ ([M^+]) 382.1721, found 382.1712.

General procedure for the preparation of the trisubstituted α,β-unsaturated sulfones (25): A mixture of the corresponding α,β-unsaturated sulfone **23** (0.4 mmol), silver carbonate (0.8 mmol, 200 mol%), $Pd(OAc)_2$ (0.04 mmol, 10 mol%), phenyl iodide (1.2 mmol, 300 mol%), and DMF (2 mL) was heated at 120 °C under vigorous stirring and argon atmosphere for 30 h. The mixture was allowed to cool to room temperature, diluted with Et_2O (20 mL), filtered through celite, washed with water (20 mL), dried ($MgSO_4$), and evaporated. The residue was purified by flash chromatography to afford **25** (the eluent and yield are indicated below for each case).

(*E*)-1-[2-(*N*,*N*-dimethylamino)phenylsulfonyl]-3-methyl-2-phenyl-1-butene (25a): Eluent hexane/ethyl acetate (10:1), 85% yield. ^{1}H NMR (200 MHz): $\delta = 8.13$ (dd, $J = 1.6$ and 7.8 Hz, 1H), 7.59 (m, 1H), 7.40 (dd, $J = 1.1$ and 8.1 Hz, 1H), 7.36–7.27 (m, 5H), 7.18–7.09 (m, 1H), 6.47 (s, 1H), 3.77 (m, 1H), 2.76 (s, 6H), 0.85 ppm (d, $J = 7.0$ Hz, 6H); ^{13}C NMR (50 MHz): $\delta = 161.5$, 154.1, 139.5, 138.5, 134.2, 130.6, 129.1, 127.9, 127.8, 125.2, 123.7, 46.0, 29.1, 20.6 ppm; HRMS (FAB+): calcd for $C_{19}H_{24}NO_2S$ ([$M+H]^+$) 330.1528, found 330.1530.

(*E*)-1-[2-(*N*,*N*-dimethylamino)phenylsulfonyl]-2-phenyl-1-heptene (25c): Eluent hexane/ethyl acetate (15:1), 70% yield. ^{1}H NMR (200 MHz): $\delta = 8.14$ (dd, $J = 1.6$ and 7.8 Hz, 1H), 7.55 (m, 1H), 7.42–7.27 (m, 7H), 6.81 (s, 1H), 2.84 (m, 4H), 2.74 (s, 6H), 1.05 (m, 4H), 0.73 ppm (m, 3H); ^{13}C NMR (75 MHz): $\delta = 155.8$, 154.0, 139.7, 139.5, 134.2, 129.4, 129.2, 129.1, 128.7, 126.5, 125.2, 123.9, 46.1, 31.7, 30.0, 27.8, 22.3, 13.9 ppm; HRMS (FAB+): calcd for $C_{21}H_{28}NO_2S$ ([$M+H]^+$) 358.1841, found 358.1847.

(*E*)-1-[2-(*N*,*N*-dimethylamino)phenylsulfonyl]-2,2-diphenylethene (25e): Eluent hexane/diethyl ether (10:1), 80% yield. M.p. 132–134 °C; ^{1}H NMR (300 MHz): $\delta = 7.49-7.46$ (m, 2H), 7.40–7.23 (m, 8H), 7.20–7.16 (m, 2H), 7.03–6.93 (m, 3H), 2.77 ppm (s, 6H); ^{13}C NMR (75 MHz): $\delta = 153.2$, 152.2, 139.6, 135.6, 133.9, 130.1, 129.8, 129.7, 129.6, 128.5, 128.3, 128.2, 128.0, 127.4, 124.8, 123.2, 46.2 ppm; HRMS (FAB+): calcd for $C_{21}H_{28}NO_2S$ ([$M+H]^+$) 364.1371, found 364.1386.

Acknowledgements

Financial support of this work by the Ministerio de Ciencia y Tecnología (BQU2000–0226) is gratefully acknowledged. P. M. also thanks the Ministerio de Ciencia y Tecnología for a predoctoral fellowship.

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[15] Although smaller quantities of Ag_2CO_3 (100 mol%) and $Pd(OAc)_2$ (2 mol%) can be used in the domino arylation of **1a**, both the conversion and the **4a**:**3a** selectivity decreased significantly.

[16] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151679 (for **4a**), CCDC-151680 (for **4e**), and CCDC-181908 (for **4h**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[17] We have noticed a slow isomerization of **3b** to allyl phenyl sulfone even in a pure state at room temperature. In fact, to completely suppress the formation of allyl phenyl sulfone, **3b** must be kept in the freezer once it has been purified by chromatography.

[18] Dihydrophenanthrenes **4** can be routinely obtained with purities of 88–97% after flash chromatography. In most cases complete elimination of the minor Heck product was achieved by further recrystallization from diethyl ether.

[19] Very significant characterization data of the dihydrophenanthrenes **4** are the molecular peak determined by MS (FAB ionization) and the chemical shifts of C9, C10, H9, and H10 in their ^{13}C and ^{1}H NMR spectra. On the other hand, in all cases the small value of $J_{9,10}$ (1.1–1.9 Hz in $CDCl_3$) is characteristic of the *trans* stereochemistry at C9/C10. This feature is also supported by the dihedral angle value determined by X-ray analysis of **4a** and **4e** (H9-C9-C10-H10 = -61.2^0 for **4a** and -69.7^0 for **4e**).

[20] For the isolation of five-membered carbon substituted palladacycles, see, for instance: a) C. Fernández-Rivas, D. J. Cárdenas, B. Martín-Matute, A. Monge, E. Gutiérrez-Puebla, A. M. Echavarren, *Organometallics* **2001**, *20*, 2998, and references therein; b) M. Oesteich, P. R. Dennison, J. K. Kodanko, L. E. Overman, *Angew. Chem.* **2001**, *113*, 1485; *Angew. Chem. Int. Ed.* **2001**, *40*, 1439; c) C. Mateo, C. Fernández-Rivas, D. J. Cárdenas, A. M. Echavarren, *Organometallics* **1998**, *17*, 3661; d) C. Mateo, D. J. Cárdenas, C. Fernández-Rivas, A. M. Echavarren, *Chem. Eur. J.* **1996**, *2*, 1596; e) C.-H. Liu, C.-S. Li, C.-H Cheng, *Organometallics* **1994**, *13*, 18.

[21] Review on organopalladium(IV) chemistry: A. J. Canty, *Acc. Chem. Res.* **1992**, *25*, 83.

[22] For Pd^{IV} five-membered palladacycles, see for instance: a) M. Catellani, G. P. Chiusoli, M. Costa, *J. Organomet. Chem.* **1995**, *500*, 69; b) G. Bocelli, M. Catellani, S. Ghelli, *J. Organomet. Chem.* **1993**, *458*, C12; c) M. Catellani, B. E. Mann, *J. Organomet. Chem.* **1990**, *390*, 251; d) see also reference [10]. For the isolation and X-ray structure of an arylpalladium(IV) five-membered palladacycle, see: e) J. M. Brunel, M.-H. Hirlemann, A. Heumann, G. Buono, *Chem. Commun.* **2000**, 1869.

[23] For a mechanistic alternative avoiding Pd^{IV} intermediates, but requiring ligand-exchange reactions between two Pd^{II} complexes, see: G. Dyker, *Chem. Ber.* **1994**, *127*, 739.

[24] For the isolation of seven-membered palladacycles, see: A. S. K. Hashmi, A. R. Nass, J. W. Bats, M. Bolte, *Angew. Chem.* **1999**, *111*, 3565; *Angew. Chem. Int. Ed.* **1999**, *38*, 3370.

[25] Unlike the reaction with *p*-iodotoluene, the reaction with *o*-iodotoluene and *m*-iodotoluene afforded complex mixtures of products.

[26] In the structural elucidation of compounds **17** and **18** the chemical shifts and coupling constants of the aromatic protons of the dihydrophenanthrene unit are particularly interesting. Compound **17** ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.53$ (d, $J = 8.1$ Hz; H_5), 7.20 (dd, $J =$ 1.8 and 8.1 Hz; H_6), 6.96 (br s; H_4), 6.92 ppm (br s, 1H; H_2). Compound **18** ^1H NMR (500 MHz, $CDCl_3$): $\delta = 8.19$ (br s; H_4), 8.15 (br d, $J =$ 8.4 Hz; H_6), 7.95 (d, $J = 8.4$ Hz; H_5), 7.88 (br s; H_2), 7.76 ppm (br s; H_8).

[27] *cis*-**1h** was prepared by photochemical stereoselective iodosulfonylation of *p*-tolylacetylene (I_2, $NaPhSO_2$, $h\nu$) and reductive cleavage of the C–I bond (58% overall yield) following the procedure described in the literature for the preparation of *cis*-**1e**: a) G. L. Edwards, C. A. Muldoon, D. J. Sinclair, *Tetrahedron* **1996**, *52*, 7779; b) W. E. Truce, G. C Wolf, *J. Org. Chem.* **1971**, *36*, 1727.

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[29] Significant ^1H NMR data of compound **19** (500 MHz, $CDCl_3$): $\delta = 7.65$ (br d, $J = 7.9$ Hz; H_5), 7.38 (dt, $J = 2.0$ and 6.9 Hz; H_6), 7.22 (dt, $J = 0.9$ and 7.3 Hz; H_7), 6.95 ppm, (br s; H_2). On the other hand, according to the mechanistic proposal for the palladium-catalyzed arylation of *cis*-substituted α,β-unsaturated phenyl sulfones (Scheme 9), both diastereomeric alkenes *trans*-**1e** and *cis*-**1e** afforded the same C9/C10 *trans* substituted dihydrophenanthrene **4e** (82% and 68% yields, respectively) in the reaction with PhI/Ag_2CO_3.

[30] The *E* stereochemistry of several trisubstituted olefins **3** and **25** was unequivocally established by NOESY experiments.

[31] For a related coordination control in Heck reactions of 2-pyridyldimethylsilyl-substituted alkenes, see: a) K. Itami, T. Nokami, Y. Ishimura, K. Mitsudo, T. Kamei, J.-I. Yoshida, *J. Am. Chem. Soc.* **2001**, *123*, 11577; b) K. Itami, T. Nokami, J.-I. Yoshida, *J. Am. Chem. Soc.* **2001**, *123*, 5600; c) K. Itami, K. Mitsudo, T. Kamei, T. Koike, T. Nokami, J.-I Yoshida,. *J. Am. Chem. Soc.* **2000**, *122*, 12013. For Pd–N coordinated complexes in Heck reaction of nitrogen-containing vinyl ethers, see: d) P. Nilsson, M. Larhed, A. Hallberg, *J. Am. Chem. Soc.* **2001**, *123*, 8217; e) M. Larhed, C. Andersson, A. Hallberg, *Tetrahedron* **1994**, *50*, 285; f) see also ref. [5].

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Received: May 10, 2002
Revised: November 29, 2002 [F4080]

  0947-6539/03/0907-1520 $ 20.00+.50/0