A Convenient Synthesis of Alkyl- and Dialkylphenanthren-9-ylamines

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Abstract: A variety of alkyl- and dialkylphenanthren-9-ylamines **1** and **2** have been prepared by radical-mediated cyclizations of the corresponding diaryleneamines **3** issued from Horner reactions between appropriate phosphorylated dibenzylamines **4** and halogenoarylaldehydes **5**.

Key words: aminophenanthrenes, carbanions, Horner reactions, radical reactions, cyclizations

9-*N*-Alkyl- and 9-*N*,*N*-dialkylaminophenanthrenes represent a class of aromatic amines which are considered as valuable building blocks for the synthesis of architecturally sophisticated natural products. In particular, they are involved in the elaboration of a variety of lignans[1] but equally of dioxoaporphines[2] and aristolactam[3] alkaloids. The recent and elegant syntheses of the synthetically challenging natural products steganone,[1] cepharadione[2] and piperolactam C[3] emphasize the potential of these polycyclic aromatic amines. Paradoxically, despite the fact that these compounds gain interest as target products of synthetic organic methodologies, they still remain accessible only by a few limited methods. The basic strategies generally involve the displacement of a variety of nucleofuges from the 9-position of a preformed phenanthrene ring system, namely bromo,[4] cyano[5] and hydroxy[2,6] groups, by the amine functionality. However, the most convenient routes are based upon the Curtius rearrangement of azides[7] and the Bischler–Napieralski cyclization of biphenyl acetamide derivatives.[2,8] More reliable methods involving the rearrangement of polycondensed triazolyl derivatives,[9] the transformation of spiro-fluorenetriazolines by electrochemical means,[10] the photochemically induced or radical-mediated cyclization of 1,2-diarylaminoethylenes,[1,11] the dehydromethoxylation of aminomethoxydihydrophenanthrenes[12] have been also reported. However, all these synthetic routes suffer from several drawbacks and genuinely lack universality. Thus, the initially mentioned synthetic methods do not solve the problems set out by the construction of poly and diversely substituted model compounds. The Bischler–Napieralski protocol can only be performed with tertiary amides and the obtention of 9-*N*-monoalkylated aminophenanthrenes necessitates an additional two step procedure involving conversion into phenanthrols and subsequent Bucherer amination reaction.[2] Moreover, this procedure requires the tedious and low yielding preparation of biaryl precursors and even though an alternative and shorter route to these parent compounds has been recently developed, all examples elaborated by this method are invariably alkoxylated at the 1-position of the phenanthrene unit.[2] At last the latter methods require harsh conditions and have been mainly confined to the construction of unsubstituted model compounds. All these limitations, in conjunction with the need for photolysis or electrolysis equipment, have provided increasing incentives to search for alternatives to these methodologies.

In our continuing study aimed at the involvement of α-aminocarbanionic species in the synthesis of alkaloids and natural products[13–16] we wish to report here an alternative and versatile synthesis of *N*-alkyl- and *N*,*N*-dialkylaminophenanthrenes **1** and **2**, respectively. Our approach, which is depicted in the retrosynthetic analysis in Scheme 1 hinges upon the oxidative radical-mediated cyclization of the halogenostilbenic amine intermediates **3** (X or Y = halogen) to generate the phenanthrene ring system. Subsequent *N*-deprotection of the annulated products **2** gives an entry to the *N*-alkylaminophenanthrenes **1** which could be used for further synthetic planning. Of central importance was the development of a synthetic route to the diarylethylene amines **3** securing the *E*-configuration required for efficient free radical cyclization. Since Horner reaction on related systems has proved to be the method of choice for the stereoselective formation of *E*-isomers[17] we therefore planned to prepare the parent enamines **3** according to the reaction between the phosphorylated benzylamine derivatives **4** (Y = halogen or H) and suitably substituted arylaldehydes **5** (X = H or halogen).

Since the position of the halogen atom on one or the other aromatic unit of the two partners involved in the assemblage of the diarylaminoethylenes by the Horner protocol was not *a priori* critical for the success of our strategy, we started the synthesis with the preparation of the phosphorylated dibenzylamine derivative **4a** (Scheme 2, Table 1 and Table 2). This compound was readily obtained by a Mannich type condensation involving three different components, *i.e.* the bromobenzaldehyde derivative **6a**, benzylamine **7** and diphenylphosphane oxide **10**.[18] Unfortunately, all attempts to metallate this phosphorylated amine with a variety of bases which allow for the survival of the bromine atom on the aromatic nucleus, e.g. LDA, KDA, KHMDS, LTMP, met with no success. We suspect

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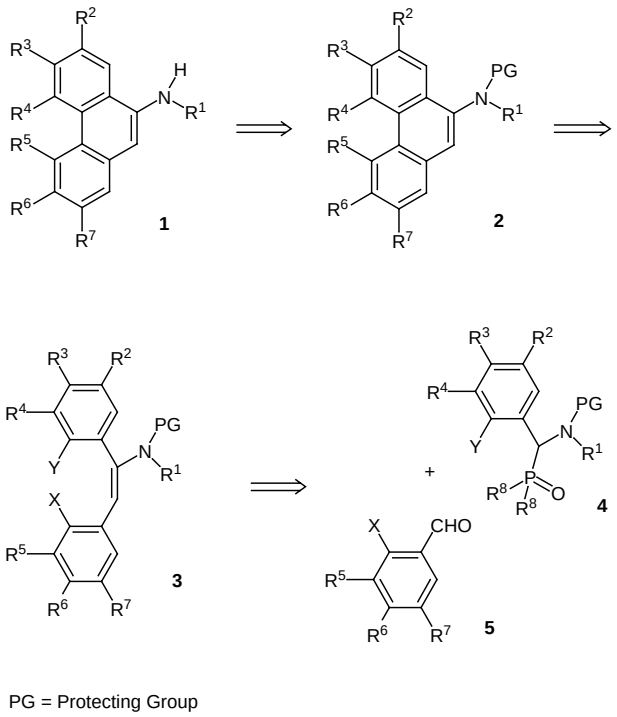
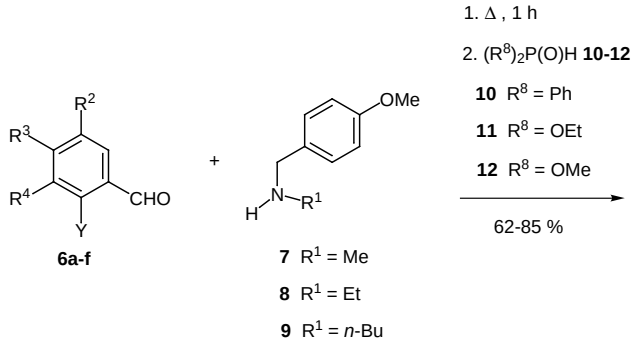
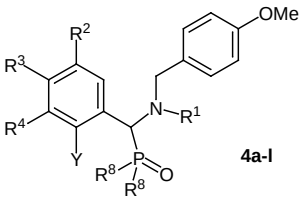


Scheme 1

the deprotonation process to be sensitive to the steric congestion of the model compounds, a phenomenon precedented at structurally similar compounds.[19] Accordingly, we set out to achieve the synthesis of enamines **3a**–**l** (Y = H, X= halogen) by introducing the halogen substitution in the "southern" aromatic part of the model compounds through the intermediacy of the halogenated arylaldehydes **5a**–**f**. An array of phosphorylated dibenzylamine derivatives **4b**–**l** was then prepared according to the above-mentioned procedure. It is worth mentioning that this protocol gives likewise access to the diphenylphosphane oxides **4b**–**h** and the phosphonic acid esters **4i**–**l** (Scheme 2, Table 1 and Table 2). Compounds **4b**–**h** and **4i**–**l** were smoothly deprotonated with butyllithium or *t*-butyllithium, respectively, in THF at –78 °C. Subsequent reaction with the *o*-halogeno aromatic aldehydes **5a**–**f** followed by warming to room temperature to ensure completion of the reaction and usual work up delivered enamines **3a**–**l** (Scheme 3, Table 3). Such compounds are usually





Scheme 2

Table 1 Phosphorylated Dibenzylamine Derivatives **4a**–**l** Prepared

Starting Aldehyde	R^1	R^2	R^3	R^4	Y	Phosphorylated Amines **4**		
							R^8	Yield (%)
6a	Me	H	OMe	OMe	Br	**4a**	Ph	70
6b	Me	H	H	H	H	**4b**	Ph	75
6c	Me	H	OMe	H	H	**4c**	Ph	77
6d	Me	OMe	OMe	H	H	**4d**	Ph	78
6e	Me	-OCH_2O-		H	H	**4e**	Ph	78
6f	Me	OMe	OMe	OMe	H	**4f**	Ph	85
6c	Et	H	OMe	H	H	**4g**	Ph	82
6c	Bu	H	OMe	H	H	**4h**	Ph	75
6d	Me	OMe	OMe	H	H	**4i**	OEt	66
6e	Me	-OCH_2O-		H	H	**4j**	OEt	62
6c	Et	H	OMe	H	H	**4k**	OMe	71
6c	Bu	H	OMe	H	H	**4l**	OMe	65

obtained by treatment of the sodium salts derived from aromatic aminonitriles with halogenobenzyl chlorides[20] or by reaction of deoxybenzoins with secondary amines.[1] They have been used as key intermediates for the preparation of natural products or pharmacologically interesting compounds.[20]

Table 2 Spectroscopic and Physical Data of the Phosphorylated Dibenzylamine Derivatives **4a**–**l**

Product	Mp (°C)	^{1}H NMR ($CDCl_3$/TMS) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ, *J* (Hz)	^{31}P NMR δ
4a	145–146	2.30 (s, 3 H, NCH_3), 3.54 (d, 1 H, *J* = 13.0, C*H*$_2$Ar), 3.71 (s, 3 H, OCH_3), 3.82 (s, 6 H, 2 × OCH_3), 3.97 (d, 1 H, *J* = 13.0, C*H*$_2$Ar), 5.34 (d, 1 H, *J* = 12.0, NCHP), 6.65 (d, 2 H_{arom}, *J* = 8.6), 6.79 (d, 2 H_{arom}, *J* = 8.6), 6.87 (d, 1 H_{arom}, *J* = 8.8), 7.22–7.27 (m, 3 H_{arom}), 7.52–7.60 (m, 5 H_{arom}), 7.99–8.05 (m, 3 H_{arom})	39.2 (d, J_{CP} = 6), 55.2, 55.9, 59.7 (d, J_{CP} = 9), 60.3, 64.6 (d, J_{CP} = 88), 110.5, 113.3, 123.1 (d, J_{CP} = 10), 124.3 (d, J_{CP} = 6), 128.0 (d, J_{CP} = 11), 128.3 (d, J_{CP} = 11), 128.4 (d, J_{CP} = 4), 129.6, 130.8 (d, J_{CP} = 9), 131.3 (d, J_{CP} = 4), 131.4, 131.5 (d, J_{CP} = 4), 131.6 (d, J_{CP} = 8.5), 132.3 (d, J_{CP} = 94), 132.9 (d, J_{CP} = 99), 146.1, 153.3, 158.4	32.4
4b	149–150	2.48 (s, 3 H, NCH_3), 3.27 (d, 1 H, *J* = 12.1, C*H*$_2$Ar), 3.75 (d, 1 H, *J* = 12.1, C*H*$_2$Ar), 3.80 (s, 3 H, OCH_3), 4.40 (d, 1 H, *J* = 11.4, NCHP), 6.71 (d, 2 H_{arom}, *J* = 8.6), 6.84 (d, 2 H_{arom}, *J* = 8.6), 7.11–7.69 (m, 13 H_{arom}), 7.80–7.95 (m, 2 H_{arom})	40.0 (d, J_{CP} = 4), 56.2, 59.6 (d, J_{CP} = 11), 65.7 (d, J_{CP} = 87), 113.5, 127.9 (d, J_{CP} = 9.5), 128.0, 128.2 (d, J_{CP} =11), 130.1, 130.8, 130.9 (d, J_{CP} = 10), 131.1 (d, J_{CP} = 3), 131.3 (d, J_{CP} = 3), 131.6 (d, J_{CP} = 8.5), 131.8 (d, J_{CP} = 9), 132.5 (d, J_{CP} = 102), 132.8 (d, J_{CP} = 96), 144.6, 158.5	32.2
4c	162–163	2.45 (s, 3 H, NCH_3), 3.26 (d, 1 H, *J* = 14.1, C*H*$_2$Ar), 3.69 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 3.75 (d, 1 H, *J* = 14.1, C*H*$_2$Ar), 4.39 (d, 1 H, *J* = 11.9, NCHP), 6.69 (d, 2 H_{arom}, *J* = 8.6), 6.80 (d, 2 H_{arom}, *J* = 8.6), 6.81 (d, 2 H_{arom}, *J* = 8.6), 7.10–7.26 (m, 3 H_{arom}), 7.46–7.52 (m, 7 H_{arom}) 7.83–7.89 (m, 2 H_{arom})	39.9 (d, J_{CP} = 4), 55.1, 55.2, 59.5 (d, J_{CP} = 11), 64.9 (d, J_{CP} = 88), 113.4, 113.5, 122.8 (d, J_{CP} = 3), 128.1 (d, J_{CP} = 11), 128.2 (d, J_{CP} = 11), 130.0, 130.1 (d, J_{CP} = 8), 130.9, 131.1 (d, J_{CP} = 3), 131.3 (d, J_{CP} = 3), 131.7 (d, J_{CP} = 9), 131.9 (d, J_{CP} = 8), 132.7 (d, J_{CP} = 94), 133.0 (d, J_{CP} = 99), 158.6, 159.2	32.3
4d	201–202	2.35 (s, 3 H, NCH_3), 3.25 (d, 1 H, *J* = 13.2, C*H*$_2$Ar), 3.75 (d, 1 H, *J* = 13.2, C*H*$_2$Ar), 3.77 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 4.30 (d, 1 H, *J* = 11.5, NCHP), 6.69 (d, 2 H_{arom}, *J* = 11.2), 6.77 (d, 1 H_{arom}, *J* = 8.4), 6.81 (d, 2 H_{arom}, *J* = 11.2), 6.95 (dd, 1 H_{arom}, *J* = 8.4, 1.9), 7.20–7.30 (m, 4 H_{arom}), 7.38–7.62 (m, 5 H_{arom}), 7.80–7.86 (m, 2 H_{arom})	40.0 (d, J_{CP} = 4), 55.2, 55.6, 55.9, 59.5 (d, J_{CP} = 11), 65.2 (d, J_{CP} = 88), 110.4, 113.4, 114.6 (d, J_{CP} = 7), 124.3 (d, J_{CP} = 9), 124.3 (d, J_{CP} = 4), 128.0 (d, J_{CP} = 11), 128.2 (d, J_{CP} = 10), 130.0, 130.9, 131.0 (d, J_{CP} = 8), 131.1 (d, J_{CP} = 3), 131.3 (d, J_{CP} = 3), 131.7 (d, J_{CP} = 8.5), 132.2 (d, J_{CP} = 99), 132.7 (d, J_{CP} = 94), 148.3, 148.6, 158.6	32.2
4e	129–130	2.35 (s, 3 H, NCH_3), 3.25 (d, 1 H, *J* = 13.2, C*H*$_2$Ar), 3.65 (d, 1 H, *J* = 13.2, C*H*$_2$Ar), 3.70 (s, 3 H, OCH_3), 4.30 (d, 1 H, *J* = 12.0, NCHP), 5.92 (s, 2 H, OCH_2O), 6.70 (d, 2 H_{arom}, *J* = 9.6), 6.71 (d, 1 H_{arom}, *J* = 9.1), 6.80 (d, 2 H_{arom}, *J* = 9.6), 6.92 (dd, 1 H_{arom}, *J* = 9.1, 2.0), 7.20–7.60 (m, 9 H_{arom}), 7.75–7.85 (m, 2 H)	39.9 (d, J_{CP} = 4.5), 55.2, 59.5 (d, J_{CP} = 11), 65.2 (d, J_{CP} = 89), 100.0, 107.8, 111.7 (d, J_{CP} = 7), 113.5, 124.4 (d, J_{CP} = 4), 125.3 (d, J_{CP} = 8.5), 128.1 (d, J_{CP} = 10), 128.2 (d, J_{CP} = 10), 130.0, 130.8, 131.1 (d, J_{CP} = 8), 131.15 (d, J_{CP} = 2.5), 131.3 (d, J_{CP} = 2.5), 131.7 (d, J_{CP} = 9), 132.5 (d, J_{CP} = 102), 132.9 (d, J_{CP} = 100), 147.2, 147.4, 158.5	32.2
4f	132–133	2.45 (s, 3 H, NCH_3), 3.29 (d, 1 H, *J* = 13.2, CH_2Ar), 3.70 (s, 3 H, OCH_3), 3.72 (d, 1 H, *J* = 13.2, C*H*$_2$Ar), 3.74 (s, 6 H, 2 × OCH_3), 3.77 (s, 3 H, OCH_3), 4.29 (d, 1 H, *J* = 11.3, NCHP), 6.66 (d, 2 H_{arom}, *J* = 8.6), 6.72 (s, 2 H_{arom}), 6.79 (d, 2 H_{arom}, *J* = 8.6), 7.14–7.22 (m, 3 H_{arom}), 7.42–7.51 (m, 5 H_{arom}), 7.79–7.85 (m, 2 H_{arom})	40.0 (d, J_{CP} = 4), 55.1, 56.2, 59.6 (d, J_{CP} = 11), 60.8, 65.8 (d, J_{CP} = 87), 108.9 (d, J_{CP} = 8), 113.5, 126.7 (d, J_{CP} = 3), 128.0 (d, J_{CP} = 11), 128.2 (d, J_{CP} = 11), 130.0, 130.7, 130.9 (d, J_{CP} = 8), 131.1 (d, J_{CP} = 3), 131.4 (d, J_{CP} = 3), 131.7 (d, J_{CP} = 8.5), 132.6 (d, J_{CP} = 95), 152.6, 158.6	32.3
4g	131–132	0.95 (t, 3 H, *J* = 7.0, CH_3), 2.20–2.26 (m, 1 H, NCH_2), 3.06 (d, 1 H, *J* = 13.5, C*H*$_2$Ar), 3.36–3.43 (m, 1 H, NCH_2), 3.75 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 4.11 (d, 1 H, *J* = 13.5, C*H*$_2$Ar), 4.39 (d, 1 H, *J* = 12.8, NCHP), 6.70 (d, 2 H_{arom}, *J* = 8.5), 6.80–6.85 (m, 4 H_{arom}), 7.27–7.29 (m, 3 H_{arom}), 7.40–7.55 (m, 7 H_{arom}), 7.76–7.83 (m, 2 H_{arom})	13.7, 45.4 (d, J_{CP} = 5), 55.1, 55.2, 54.8 (d, J_{CP} = 9), 113.4, 123.7 (d, J_{CP} = 3), 128.0 (d, J_{CP} = 11), 128.1 (d, J_{CP} = 11), 130.1, 130.9, (d, J_{CP} = 8), 131.2, 131.5, 132.0 (d, J_{CP} = 8), 132.4 (d, J_{CP} = 99), 132.8 (d, J_{CP} = 7), 132.8 (d, J_{CP} = 95), 158.4, 159.1	32.5

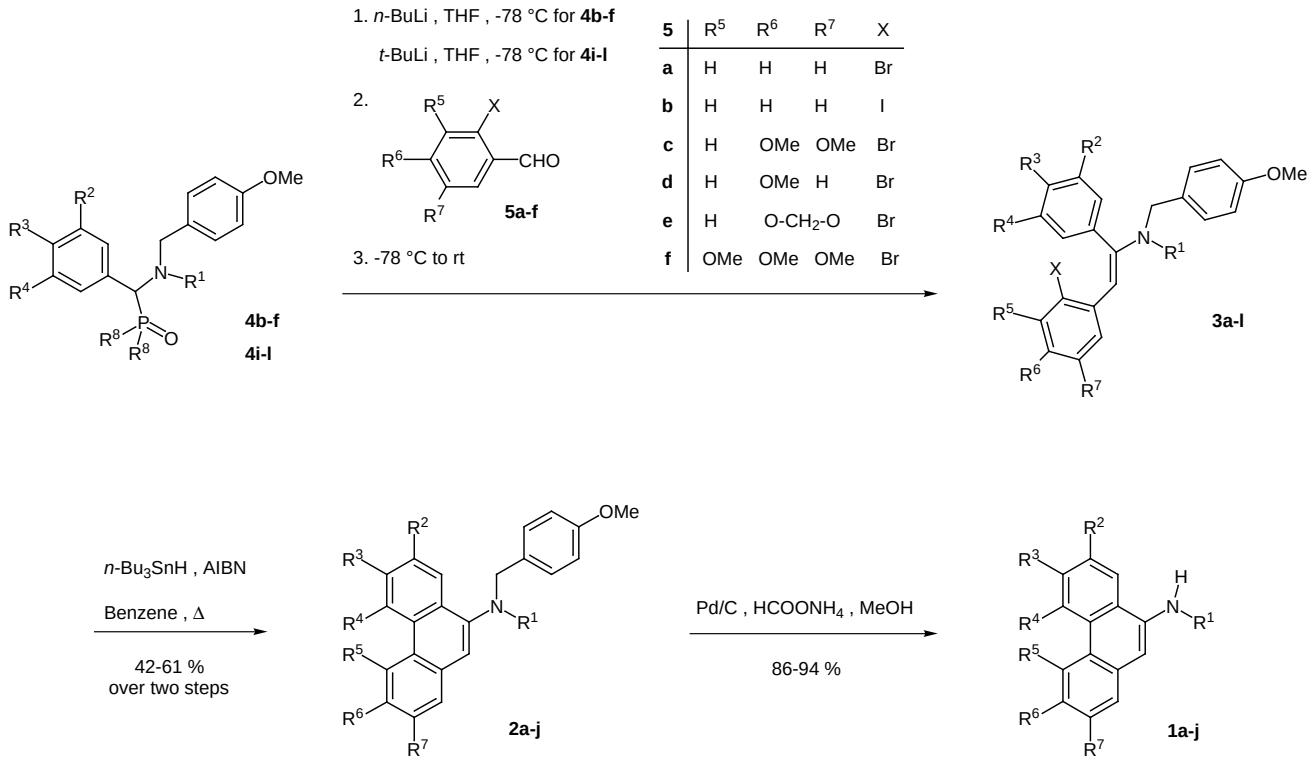
Table 2 Spectroscopic and Physical Data of the Phosphorylated Dibenzylamine Derivatives **4a**–**l** (continued)

Product	Mp (°C)	^{1}H NMR ($CDCl_3$/TMS) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ, *J* (Hz)	^{31}P NMR δ
4h	114–115	0.90 (t, 3 H, *J* = 6.4, CH_3), 1.20–1.22 (m, 2 H, CH_2), 1.23–1.40 (m, 2 H, CH_2), 2.19–2.22 (m, 1 H, NCH_2), 3.05 (d, 1 H, *J* = 13.4, C*H*$_2$Ar), 3.27 (m, 1 H, NCH_2), 3.75 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 4.13 (d, 1 H, *J* = 13.4, C*H*$_2$Ar), 4.40 (d, 1 H, *J* = 12.4, NCHP), 6.72 (d, 2 H_{arom}, *J* = 8.8), 6.81 (d, 2 H_{arom}, *J* = 8.8), 6.78–6.84 (m, 2 H_{arom}), 7.14–7.30 (m, 3 H_{arom}), 7.35–7.58 (m, 7 H_{arom}), 7.71–7.83 (m, 2 H_{arom})	14.2, 20.2, 30.5, 51.1, 51.2, 55.1, 55.2, 59.5, 62.1 (d, J_{CP} = 88), 113.4, 123.6, 128.0 (d, J_{CP} = 11), 128.1 (d, J_{CP} = 11), 128.2 (d, J_{CP} = 11), 130.0, (d, J_{CP} = 9), 130.2, 131.0 (d, J_{CP} = 3), 131.3 (d, J_{CP} = 3), 131.2 (d, J_{CP} = 3), 131.5, 132.0 (d, J_{CP} = 8.5), 132.4 (d, J_{CP} = 114), 132.9 (d, J_{CP} = 7), 133.0 (d, J_{CP} = 101), 158.4, 159.1	32.2
4i	oil	1.03 (t, 3 H, *J* = 7.1, CH_3), 1.37 (t, 3 H, *J* = 7.1, CH_3), 2.40 (s, 3 H, CH_3N), 3.29 (d, 1 H, *J* = 13.0, C*H*$_2$Ar), 3.65 (d, 1 H, *J* = 13.0, C*H*$_2$Ar), 3.77 (s, 3 H, CH_3O), 3.86 (s, 6 H, 2 × CH_3O), 3.88–3.97 (m, 3 H, CH_2OP + CHP), 4.13–4.27 (m, 2 H, CH_2OP), 6.83 (d, 2 H_{arom}, *J* = 8.8), 6.84 (d, 1 H_{arom}, *J* = 8.3), 6.97 (dd, 1 H_{arom}, *J* = 8.3, 1.3), 7.04 (d, 1 H_{arom}, *J* = 1.3), 7.22 (d, 2 H_{arom}, *J* = 8.8)	16.2 (d, J_{CP} = 6), 16.5 (d, J_{CP} = 6), 39.7 (d, J_{CP} = 4.5), 55.1, 55.7, 55.8, 59.1 (d, J_{CP} = 13), 62.2 (d, J_{CP} = 7), 62.5 (d, J_{CP} = 7), 63.7 (d, J_{CP} = 163), 110.5, 113.6, 113.8 (d, J_{CP} = 8), 123.4 (d, J_{CP} = 10), 124.3 (d, J_{CP} = 4), 130.0, 130.9, 148.4, 148.7, 158.7	23.6
4j	oil	1.03 (t, 3 H, *J* = 7.1, CH_3), 1.32 (t, 3 H, *J* = 7.1, CH_3), 2.34 (s, 3 H, CH_3N), 3.26 (d, 1 H, *J* = 13.1, C*H*$_2$Ar), 3.69–3.73 (m, 2 H, C*H*$_2$Ar + CHP), 3.74 (s, 3 H, CH_3O), 3.87–3.95 (m, 2 H, CH_2OP), 4.15–4.22 (m, 2 H, CH_2OP), 5.91 (s, 2 H, OCH_2O), 6.75 (d, 1 H_{arom}, *J* = 8.7), 6.81 (d, 2 H_{arom}, *J* = 8.6), 6.84 (dd, 1 H_{arom}, *J* = 8.7, 1.4), 7.00 (d, 1 H_{arom}, *J* = 1.4), 7.21 (d, 2 H_{arom}, *J* = 8.6)	16.2 (d, J_{CP} = 6), 16.6 (d, J_{CP} = 6), 39.6 (d, J_{CP} = 5), 55.2, 59.1 (d, J_{CP} = 13), 62.2 (d, J_{CP} = 7), 62.6 (d, J_{CP} = 7), 65.9 (d, J_{CP} = 163), 101.1, 107.8, 110.9 (d, J_{CP} = 8), 113.6, 124.5 (d, J_{CP} = 10), 124.5 (d, J_{CP} = 4.5), 130.0, 130.9, 147.3, 147.4, 158.7	23.5
4k	oil	1.08 (t, 3 H, *J* = 7.0, CH_3), 2.21–2.28 (m, 1 H, NCH_2), 3.09 (d, 1 H, *J* = 13.5, C*H*$_2$Ar), 3.10–3.16 (m, 1 H, NCH_2), 3.44 (d, 3 H, *J* = 10.5, $POCH_3$), 3.75 (s, 3 H, CH_3O), 3.77 (s, 3 H, CH_3O), 3.86 (d, 3 H, *J* = 10.5, $POCH_3$), 4.05 (d, 1 H, *J* = 13.5, C*H*$_2$Ar), 4.12 (d, 1 H, *J* = 25.8, CHP), 6.84 (d, 2 H_{arom}, *J* = 8.5), 6.88 (d, 2 H_{arom}, *J* = 8.5), 7.26 (d, 2 H_{arom}, *J* = 8.5), 7.38 (d, 2 H_{arom}, *J* = 8.5)	13.4, 44.7 (d, J_{CP} = 7), 52.4 (d, J_{CP} = 7), 53.9 (d, J_{CP} = 7), 54.3 (d, J_{CP} = 10), 55.1, 55.2, 59.7 (d, J_{CP} = 164), 113.5, 113.6, 124.1 (d, J_{CP} = 6), 130.0, 131.6, 131.9 (d, J_{CP} = 9), 158.6, 159.3	26.4
4l	oil	0.80 (t, 3 H, *J* = 7.1, CH_3), 1.21–1.35 (m, 4 H, 2 × CH_2), 2.18–2.22 (m, 1 H, NCH_2), 3.00–3.04 (m, 1 H, NCH_2), 3.07 (d, 1 H, *J* = 13.4, C*H*$_2$Ar), 3.41 (d, 3 H, *J* = 10.4, $POCH_3$), 3.74 (s, 3 H, CH_3O), 3.76 (s, 3 H, CH_3O), 3.82 (d, 3 H, *J* = 10.5, $POCH_3$), 4.05 (d, 1 H, *J* = 13.4, C*H*$_2$Ar), 4.09 (d, 1 H, *J* = 26.0, CHP), 6.82 (d, 2 H_{arom}, *J* = 8.5), 6.86 (d, 2 H_{arom}, *J* = 8.5), 7.24 (d, 2 H_{arom}, *J* = 8.5), 7.36 (d, 2 H_{arom}, *J* = 8.5)	14.0, 20.2, 30.3, 50.3 (d, J_{CP} = 7), 52.4 (d, J_{CP} = 7), 53.6 (d, J_{CP} = 7), 54.6 (d, J_{CP} = 10), 55.1, 55.15, 59.7 (d, J_{CP} = 164), 113.5, 113.6, 124.1 (d, J_{CP} = 6), 130.0, 131.6, 132.0 (d, J_{CP} = 9), 158.6, 159.3	26.5

[a] Satisfactory microanalyses obtained: C ±0.29, H ±0.27, N ±0.31.

Once again the Horner reaction seems to be sensitive to the steric congestion of the parent phosphorylated dibenzylamines since its application to the bulkier diphenylphosphane oxides **4g**,**h** failed to give the expected enamines **3i**,**j** even though **4g**,**h** could be successfully deprotonated with BuLi (D incorporation after D_2O quenching). However, enamines **3i**,**j** were gratifyingly obtained starting from less hindered dimethoxyphosphoryl derivatives **4k**,**l** by making use of *t*-BuLi as the base (Scheme 3, Table 3).

The configuration of the double bond was established by NOE experiments and above all by comparison of the chemical shift of the olefinic protons of **3a**–**l** (5.55 ± 0.05 ppm) with that calculated for the *E*- and *Z*-isomers (5.6 and 6.0 ppm, respectively) using the substituent shielding constants.[21] It is worth noting that the exclusively formed isomers were uniformly of the *E*-structure, regardless of the degree of substitution of these model compounds, the nature of the halogen substituent and of the temporarily activating phosphorylated agent. Since a marked tendency of enamines to undergo hydrolysis under standard isolation treatments was observed they were directly submitted to the well documented oxidative radical cyclization conditions.[22] The radical reaction was performed by slow dropwise addition of a benzene solution of tributyltin hydride and AIBN to a refluxing benzene solution of **3a**–**l** under argon. This protocol delivered the fused dialkylaminophenanthrenes **2a**–**j** with satisfactory yields (Scheme3,



5	R^5	R^6	R^7	X
a	H	H	H	Br
b	H	H	H	I
c	H	OMe	OMe	Br
d	H	OMe	H	Br
e	H	O-CH_2-O		Br
f	OMe	OMe	OMe	Br

Scheme 3

Table 3 and Table 4). Interestingly, the radical-mediated cyclization process turned out highly regioselective since cyclocondensations of compounds **3f**,**g**, which are liable to furnish mixtures of regioisomers, afforded exclusively the single isomers **2f**,**g**. The final removal of the *p*-methoxybenzyl protection of the amino group proved more problematic than we had anticipated. This may probably be due to the fact that the 9,10 carbon–carbon bond of the

Table 3 Enamines **3a**–**l**, Dialkylphenanthren-9-ylamines **2a**–**j** and Alkylphenanthren-9-ylamines **1a**–**j** Prepared

R^1	R^2	R^3	R^4	R^5	R^6	R^7	X	Starting Materials	Enamine **3**	Amine **2** Yield (%)[a]		Amine **1** Yield (%)	
Me	H	H	H	H	H	H	Br	**4b** + **5a**	**3a**	**2a**	44	**1a**	92
Me	H	H	H	H	H	H	I	**4b** + **5b**	**3k**	**2a**	47		
Me	H	H	H	H	OMe	OMe	Br	**4b** + **5c**	**3b**	**2b**	48	**1b**	91
Me	H	OMe	H	H	H	H	Br	**4c** + **5a**	**3c**	**2c**	42	**1c**	86
Me	H	OMe	H	H	H	H	I	**4c** + **5b**	**3l**	**2c**	45		
Me	H	OMe	H	H	OMe	H	Br	**4c** + **5d**	**3d**	**2d**	51	**1d**	89
Me	H	OMe	H	H	-OCH_2O-		Br	**4c** + **5e**	**3e**	**2e**	61	**1e**	90
Me	OMe	OMe	H	H	H	H	Br	**4d** + **5a**	**3f**	**2f**	55	**1f**	88
Me	OMe	OMe	H	H	H	H	Br	**4i** + **5a**	**3f**	**2f**	57		
Me	-OCH_2O-		H	H	H	H	Br	**4e** + **5a**	**3g**	**2g**	52	**1g**	92
Me	-OCH_2O-		H	H	H	H	Br	**4j** + **5a**	**3g**	**2g**	55		
Me	OMe	OMe	OMe	H	OMe	H	Br	**4f** + **5d**	**3h**	**2h**	56	**1h**	94
Et	H	OMe	H	OMe	OMe	OMe	Br	**4k** + **5f**	**3i**	**2i**	57	**1i**	89
Bu	H	OMe	H	OMe	OMe	OMe	Br	**4l** + **5f**	**3j**	**2j**	48	**1j**	91

[a] Yields calculated over two steps starting from **4**.

Table 4 Spectroscopic and Physical Data of the Dialkylphenanthren-9-ylamines **2a–j** Prepared

Product[a]	Mp (°C)	^{1}H NMR ($CDCl_3$/TMS) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ, *J* (Hz)
2a	122–123	2.81 (s, 3 H, NCH_3), 3.81 (s, 3 H, OCH_3), 4.25 (s, 2 H, C*H*$_2$Ar), 6.90 (d, 2 H_{arom}, *J* = 8.7), 7.28 (s, 1 H_{arom}), 7.35 (d, 2 H_{arom}, *J* = 8.7), 7.51–7.58 (m, 2 H_{arom}), 7.62–7.70 (m, 2 H_{arom}), 7.78 (dd, 1 H_{arom}, *J* = 9.3, 3.2), 8.47 (dd, 1 H_{arom}, *J* = 7.1, 3.2), 8.62 (dd, 1 H_{arom}, *J* = 6.1, 3.5), 8.72 (dd, 1 H_{arom}, *J* = 7.5, 3.2)	41.4, 55.3, 60.4, 113.8, 115.1, 122.4, 123.1, 124.5, 125.1, 126.4, 126.5, 126.7, 127.7, 127.9, 129.5, 130.7, 131.7, 132.5, 158.8
2b	135–136	2.79 (s, 3 H, NCH_3), 3.81 (s, 3 H, OCH_3), 4.03 (s, 3 H, OCH_3), 4.10 (s, 3H, OCH_3), 4.24 (s, 2 H, C*H*$_2$Ar), 6.90 (d, 2 H_{arom}, *J* = 7.8), 7.16 (s, 1 H_{arom}), 7.24 (s, 1 H_{arom}), 7.35 (d, 2 H_{arom}, *J* = 7.8), 7.56–7.63 (m, 2 H_{arom}), 7.96 (s, 1 H_{arom}), 8.47 (d, 1 H_{arom}, *J* = 7.9), 8.55 (d, 1 H_{arom}, *J* = 7.9)	41.5, 55.3, 55.9, 56.0, 60.6, 103.4, 107.8, 113.7, 114.7, 122.1, 122.6, 124.5, 125.3, 126.2, 127.5, 128.5, 130.0, 130.7, 131.1, 146.9, 148.3, 149.5, 158.7
2c	81–82	2.80 (s, 3 H, NCH_3), 3.81 (s, 3 H, OCH_3), 4.02 (s, 3 H, OCH_3), 4.25 (s, 2 H, C*H*$_2$Ar), 6.98 (d, 2 H_{arom}, *J* = 8.5), 7.16 (s, 1 H_{arom}), 7.28–7.34 (m, 3 H_{arom}), 7.49–7.55 (m, 2 H_{arom}), 7.75 (dd, 1 H_{arom}, *J* = 9.3, 4.2), 8.07 (d, 1 H_{arom}, *J* = 2.4), 8.38 (d, 1 H_{arom}, *J* = 9.0), 8.53 (dd, 1 H_{arom}, *J* = 9.3, 4.2)	41.4, 55.3, 55.5, 60.5, 104.6, 113.0, 113.8, 116.1, 122.5, 123.5, 124.7, 126.2, 126.8, 127.8, 129.0, 129.5, 130.0, 133.1, 158.4, 158.8
2d	76–77	2.75 (s, 3 H, NCH_3), 3.80 (s, 3 H, OCH_3), 3.99 (s, 3 H, OCH_3), 4.01 (s, 3 H, OCH_3), 4.19 (s, 2 H, C*H*$_2$Ar), 6.88 (d, 2 H_{arom}, *J* = 8.5), 7.12 (s, 1 H_{arom}), 7.19 (dd, 1 H_{arom}, *J* = 8.7, 2.4), 7.33 (d, 2 H_{arom}, *J* = 8.5), 7.67 (d, 1 H_{arom}, *J* = 8.7), 7.90 (d, 1 H_{arom}, *J* = 2.4), 7.97 (d, 1 H_{arom}, *J* = 2.5), 8.39 (d, 1 H_{arom}, *J* = 9.6)	41.5, 55.5, 55.6, 60.6, 104.4, 104.9, 112.9, 113.7, 115.9, 116.5, 119.1, 124.2, 126.2, 127.7, 129.2, 129.5, 130.8, 132.5, 146.4, 157.2, 158.1, 158.7
2e	191–192	2.75 (s, 3 H, NCH_3), 3.81 (s, 3 H, OCH_3), 4.00 (s, 3 H, OCH_3), 4.20 (s, 2 H, C*H*$_2$Ar), 6.06 (s, 2 H, OCH_2O), 6.88 (d, 2 H_{arom}, *J* = 8.6), 7.06 (s, 1 H_{arom}), 7.10 (s, 1 H_{arom}), 7.21 (dd, 1 H_{arom}, *J* = 9.2, 2.6), 7.33 (d, 2 H_{arom}, *J* = 8.6), 7.80 (d, 1 H_{arom}, *J* = 2.6), 7.87 (s, 1 H_{arom}), 8.34 (d, 1 H_{arom}, *J* = 9.2)	41.6, 55.3, 55.4, 60.7, 100.9, 101.2, 103.9, 105.2, 113.2, 113.7, 115.6, 123.0, 123.1, 126.2, 127.4, 130.7, 146.7, 147.2, 147.7, 158.2, 158.8
2f	135–136	2.85 (s, 3 H, NCH_3), 3.81 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 4.12 (s, 3 H, OCH_3), 4.23 (s, 2 H, C*H*$_2$Ar), 6.90 (d, 2 H_{arom}, *J* = 8.5), 7.25 (s, 1 H_{arom}), 7.38 (d, 2 H_{arom}, *J* = 8.5), 7.46–7.53 (m, 2 H_{arom}), 7.77 (dd, 2 H_{arom}, *J* = 7.5, 2.7), 7.81 (s, 1 H_{arom}), 8.02 (s, 1 H_{arom}), 8.46 (dd, 1 H_{arom}, *J* = 7.5, 2.4)	40.9, 55.3, 55.8, 55.9, 60.6, 103.7, 104.8, 113.3, 113.8, 121.9, 124.2, 124.7, 125.8, 126.2, 127.3, 127.8, 129.1, 130.8, 132.0, 147.7, 149.1, 158.1
2g	158–159	2.75 (s, 3 H, NCH_3), 3.81 (s, 3 H, OCH_3), 4.21 (s, 2 H, C*H*$_2$Ar), 6.11 (s, 2 H, OCH_2O), 6.88 (d, 2 H_{arom}, *J* = 8.3), 7.27 (s, 1 H_{arom}), 7.34 (d, 2 H_{arom}, *J* = 8.3), 7.45–7.56 (m, 2 H_{arom}), 7.75 (dd, 1 H_{arom}, *J* = 9.3, 4.1), 7.88 (s, 1 H_{arom}), 8.05 (s, 1 H_{arom}), 8.41 (dd, 1 H_{arom}, *J* = 9.0, 2.4)	41.7, 55.2, 60.3, 100.3, 102.4, 113.7, 114.5, 122.1, 124.9, 125.9, 126.0, 127.8, 127.9, 129.6, 130.6, 131.9, 147.7, 147.9, 158.7
2h	107–108	2.81 (s, 3 H, NCH_3), 3.82 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 3.95 (s, 3 H, OCH_3), 4.01 (s, 3 H, OCH_3), 4.05 (s, 3 H, OCH_3), 4.07 (s, 3 H, OCH_3), 4.17 (s, 2 H, C*H*$_2$Ar), 6.91 (d, 2 H_{arom}, *J* = 8.3), 7.19 (dd, 1 H_{arom}, *J* = 7.7, 1.4), 7.28 (s, 1 H_{arom}), 7.39 (d, 2 H_{arom}, *J* = 8.3), 7.69 (d, 1 H_{arom}, *J* = 7.7), 7.85 (s, 1 H_{arom}), 9.07 (d, 1 H_{arom}, *J* = 1.4)	41.2, 55.3, 55.4, 55.8, 60.5, 60.7, 61.3, 101.3, 107.9, 113.8, 115.8, 116.0, 119.9, 127.8, 128.2, 128.7, 129.05, 129.1, 130.9, 142.5, 145.5, 152.4, 152.7, 157.5, 158.7
2i	91–92	1.02 (t, 3 H, *J* = 6.9, CH_3), 3.13 (q, 3 H, *J* = 6.9, NCH_2), 3.75 (s, 3 H, OCH_3), 3.97 (s, 3 H, OCH_3), 3.98 (s, 6 H, 2 × OCH_3), 4.01 (s, 3 H, OCH_3), 4.24 (s, 2 H, C*H*$_2$Ar), 6.81 (d, 2 H_{arom}, *J* = 8.5), 6.95 (s, 1 H_{arom}), 7.01 (s, 1 H_{arom}), 7.20 (dd, 1 H_{arom}, *J* = 9.1, 2.6), 7.29 (d, 2 H_{arom}, *J* = 8.5), 8.41 (d, 1 H_{arom}, *J* = 9.1), 9.08 (d, 1 H_{arom}, *J* = 2.8)	11.4, 46.5, 55.2, 55.3, 55.8, 56.8, 60.4, 61.3, 104.4, 108.0, 115.3, 115.4, 115.9, 121.4, 124.3, 125.6, 129.5, 131.0, 132.7, 145.6, 152.2, 152.5, 158.2, 158.5
2j	oil	0.88 (t, 3 H, *J* = 7.4, CH_3), 1.34 (m, 2 H, CH_2), 1.57 (m, 2 H, CH_2), 3.16 (t, 2 H, *J* = 7.4, NCH_2), 3.77 (s, 3 H, OCH_3), 4.02 (s, 3 H, OCH_3), 4.05 (s, 3 H, OCH_3), 4.08 (s, 3 H, OCH_3), 4.12 (s, 3 H, OCH_3), 4.31 (s, 2 H, C*H*$_2$Ar), 6.87 (d, 2 H_{arom}, *J* = 8.6), 7.05 (s, 1 H_{arom}), 7.15 (s, 1 H_{arom}), 7.30–7.35 (m, 3 H_{arom}), 8.56 (d, 1 H_{arom}, *J* = 9.1), 9.22 (d, 1 H_{arom}, *J* = 2.6)	14.1, 20.6, 23.3, 28.7, 51.9, 55.1, 55.3, 55.8, 58.0, 60.5, 61.3, 104.5, 108.2, 113.6, 115.4, 115.6, 116.0, 124.5, 125.6, 129.6, 130.9, 131.1, 132.9, 141.4, 145.9, 152.4, 152.6, 158.4, 158.6

[a] Satisfactory microanalyses obtained: C ±0.25, H ±0.23, N ±0.32.

phenanthrene ring system of **2a**–**j** holds simultaneously the disadvantages linked to its marked degree of double bond character which may account for its sensitivity with regard to hydrogenolysis conditions and also to its still determining enamine character. After some experimentation we found that the benzylic protection of the amino group could be easily removed with Pd on C and ammonium formate in methanol thus providing excellent yields of the desired *N*-alkylaminophenanthrenes **1a**–**j** (Table 3 and Table 5).

In summary, the goal of our program, to develop a general and versatile approach to the synthesis of *N*-alkyl and *N*,*N*-dialkylaminophenanthrenes, has been met with full success. This synthetic route, which complements the existent methodologies, offers special advantages including high efficiency, procedural simplicity, mildness of reac-

Table 5 Spectroscopic and Physical Data of the Alkylphenanthren-9-ylamines **1a**–**j** Prepared

Product[a]	Mp (°C)	^{1}H NMR ($CDCl_3$/TMS) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ, *J* (Hz)
1a	88–89[b]	–[c]	
1b	138–139	3.07 (s, 3 H, NCH_3), 4.02 (br s, 4 H, OCH_3 + NH), 4.07 (s, 3 H, OCH_3), 6.73 (s, 1 H_{arom}), 7.12 (s, 1 H_{arom}), 7.53 (dt, 1 H_{arom}, *J* = 8.1, 1.2), 7.62 (dt, 1 H_{arom}, *J* = 8.2, 1.2), 7.86 (dd, 1 H_{arom}, *J* = 8.1, 1.2), 8.00 (s, 1 H_{arom}), 8.53 (dd, 1 H_{arom}, *J* = 7.9, 1.2)	31.8, 55.8, 56.1, 101.7, 103.8, 107.0, 119.2, 120.4, 123.0, 124.5, 125.2, 126.2, 128.8, 130.5, 141.3, 146.7, 149.7
1c	94–95	3.06 (s, 3 H, NCH_3), 4.00 (s, 3 H, OCH_3), 4.30 (br s, 1 H, NH), 6.66 (s, 1 H_{arom}), 7.21 (dd, 1 H_{arom}, *J* = 9.0, 2.4), 7.38 (t, 1 H_{arom}, *J* = 7.6), 7.49 (t, 1 H_{arom}, *J* = 7.2), 7.70 (dd, 1 H_{arom}, *J* = 8.0, 2.4), 7.76 (d, 1 H_{arom}, *J* = 9.0), 8.07 (d, 1 H_{arom}, *J* = 2.4), 8.45 (dd, 1 H_{arom}, *J* = 8.0, 2.1)	31.0, 55.4, 99.9, 105.0, 115.8, 120.0, 121.8, 122.4, 124.8, 126.7, 127.0, 132.6, 134.4, 142.4, 158.3
1d	140–141	3.06 (s, 3 H, NCH_3), 3.97 (s, 3 H, OCH_3), 4.01 (br s, 4 H, OCH_3 + NH), 6.65 (s, 1 H_{arom}), 7.16 (dd, 1 H_{arom}, *J* = 8.7, 2.5), 7.22 (dd, 1 H_{arom}, *J* = 9.1, 2.5), 7.63 (d, 1 H_{arom}, *J* = 8.7), 7.81 (d, 1 H_{arom}, *J* = 9.1), 7.85 (d, 1 H_{arom}, *J* = 2.5), 7.97 (d, 1 H_{arom}, *J* = 2.5)	31.2, 55.5, 55.6, 100.2, 104.8, 105.4, 115.6, 116.6, 120.5, 122.0, 125.8, 128.0, 128.9, 140.7, 158.0
1e	178–179	3.11 (s, 3 H, NCH_3), 3.99 (br s, 4 H, OCH_3 + NH), 6.03 (s, 2 H, OCH_2O), 6.58 (s, 1 H_{arom}), 7.07 (s, 1 H_{arom}), 7.15 (dd, 1 H_{arom}, *J* = 9.0, 2.6), 7.77 (d, 1 H_{arom}, *J* = 8.0), 7.80 (s, 2 H_{arom})	31.1, 55.4, 100.6, 100.9, 104.3, 104.4, 108.5, 114.6, 118.3, 120.3, 122.4, 129.5, 132.3, 141.3, 146.1, 148.3, 150.2
1f	119–120	3.07 (s, 3 H, NCH_3), 4.01 (s, 3 H, OCH_3), 4.09 (s, 3 H, OCH_3), 4.22 (br s, 1 H, NH), 6.74 (s, 1 H_{arom}), 7.14 (s, 1 H_{arom}), 7.37 (dd, 1 H_{arom}, *J* = 7.7, 1.0), 7.42 (dd, 1 H_{arom}, *J* = 7.7, 1.0), 7.71 (dd, 1 H_{arom}, *J* = 7.7, 1.0), 7.98 (s, 1 H_{arom}), 8.37 (dd, 1 H_{arom}, *J* = 7.7, 1.0)	31.2, 55.9, 101.1, 101.15, 104.1, 120.2, 121.9, 122.6, 124.9, 125.6, 125.9, 126.8, 133.1, 141.9, 149.0
1g	155–156	3.07 (s, 3 H, NCH_3), 4.10 (br s, 1 H, NH), 6.10 (s, 2 H, OCH_2O), 6.74 (s, 1 H_{arom}), 7.24 (s, 1 H_{arom}), 7.34 (t, 1 H_{arom}, *J* = 7.9), 7.43 (d, 1 H_{arom}, *J* = 7.8), 7.70 (d, 1 H_{arom}, *J* = 7.8), 8.03 (s, 1 H_{arom}), 8.31 (d, 1 H_{arom}, *J* = 7.9)	31.2, 98.6, 101.3, 101.4, 101.7, 121.4, 122.1, 122.7, 125.2, 126.1, 126.7, 127.3, 133.1, 142.2, 147.8
1h	115–116	3.05 (s, 3 H, NCH_3), 3.97 (br s, 4 H, OCH_3 + NH), 4.01 (s, 3 H, OCH_3), 4.03 (s, 3 H, OCH_3), 4.04 (s, 3 H, OCH_3), 6.79 (s, 1 H_{arom}), 7.10 (s, 1 H_{arom}), 7.14 (d, 1 H_{arom}, *J* = 8.5), 7.63 (d, 1 H_{arom}, *J* = 8.5), 9.00 (s, 1 H_{arom})	31.5, 55.4, 55.9, 60.5, 61.3, 97.7, 103.8, 108.1, 116.1, 119.5, 124.2, 125.9, 127.7, 127.8, 139.9, 142.5, 152.4, 153.0, 156.0
1i	135–136	1.40 (t, 3 H, *J* = 7.1, CH_3), 3.33 (q, 2 H, *J* = 7.1, NCH_2), 3.96 (br s, 7 H, 2 × OCH_3 + NH), 3.97 (s, 6 H, 2 × OCH_3), 6.55 (s, 1 H_{arom}), 6.89 (s, 1 H_{arom}), 7.15 (dd, 1 H_{arom}, *J* = 9.0, 2.7), 7.77 (d, 1 H_{arom}, *J* = 9.0), 9.11 (d, 1 H_{arom}, *J* = 2.7)	14.7, 38.7, 55.2, 55.7, 60.3, 61.3, 100.6, 103.3, 108.5, 112.8, 115.0, 119.3, 121.1, 121.4, 132.2, 132.5, 139.5, 141.3, 152.4, 152.7, 158.1
1j	102–103	1.02 (t, 3 H, *J* = 7.3, CH_3), 1.55 (m, 2 H, CH_2), 1.78 (m, 2 H, CH_2), 3.30 (t, 2 H, *J* = 7.0, NCH_2) 4.00 (br s, 10 H, 3 × OCH_3 + NH), 4.01 (s, 3 H, OCH_3), 6.58 (s, 1 H_{arom}), 6.92 (s, 1 H_{arom}), 7.17 (dd, 1 H_{arom}, *J* = 9.0, 2.1), 7.78 (d, 1 H_{arom}, *J* = 9.0), 9.15 (d, 1 H_{arom}, *J* = 2.1)	14.0, 20.6, 31.6, 43.0, 55.3, 55.7, 60.4, 61.4, 100.5, 103.3, 108.6, 112.8, 115.0, 119.4, 121.0, 132.3, 132.6, 139.5, 141.4, 152.4, 152.8, 158.1

[a] Satisfactory microanalyses obtained: C ±0.27, H ±0.29, N ±0.23.
[b] Lit.[6] mp 88.5–89.5.
[c] See Ref.[32]

tion conditions and easy accessibility to the reaction partners. The versatility of this process should be rewarded by giving easy access to a wide array of natural and biologically active compounds. Further exploitation along these lines is under way in our laboratory.

Melting point determinations were carried out on a Reichert-Thermopan apparatus and were recorded uncorrected. ^{1}H, ^{13}C and ^{31}P NMR spectra were measured at 300 MHz, 75 MHz and 121 MHz, respectively, on a Bruker AM 300 spectrometer as solutions in $CDCl_3$ with TMS as internal standard or H_3PO_4 as external standard. Elemental analyses were determined at the CNRS microanalysis centre. Compounds were purified until observed as single spots on TLC (Merck Kieselgel 60 F_{254}). For flash chromatography, Merck silica gel 60 (230–400 mesh ASTM) was used. All solvents were dried and distilled according to standard procedures. Dry glassware for moisture-sensitive reactions was obtained by oven-drying and assembly under Ar. An inert atmosphere was obtained with a stream of Ar and glassware equipped with rubber septa; reagent transfer was performed by syringe. Petroleum ether refers to the fraction boiling at 40–60 °C.

The commercially available aromatic aldehydes **6b–f** and halogenated arylaldehydes **5a**,**b** were recrystallized or distilled under reduced pressure before use. The diversely substituted bromobenzaldehydes **5c**,[23] **5d**,[24] **5e**,[25] **5f**[26] and **6a**[27] and *N*-Alkyl-4-methoxybenzylamines **7**,[28] **8**[29] and **9**[30] were prepared according to already reported procedures. Diphenylphosphane oxide **10** was obtained by a known procedure.[31,32]

Phosphorylated Dibenzylamines 4a–l; General Procedure

A solution of *N*-alkylbenzylamine **7–9** (20 mmol) in toluene (10 mL) was slowly added to a cooled (0 °C) solution of the appropriate (halogeno)arylaldehyde **6a–f** (20 mmol) in toluene (20 mL) under Ar. The mixture was warmed to room temperature and then refluxed over a period of 1 h. $Ph_2P(O)H$ (**10**; 4.1 g, 20 mmol for compounds **4a**–**h**), $(EtO)_2P(O)H$ (**11**; 4.7 g, 20 mmol for compounds **4i**,**j**) or $(MeO)_2P(O)H$ (**12**; 2.7 g, 20 mmol for compounds **4k**,**l**) was then added, the mixture refluxed for an additional hour and the water formed removed by azeotropic distillation using a Dean–Stark apparatus. The solvent was removed and the crude product containing the diphenylphosphane oxide **4a**–**h** triturated with Et_2O, filtered and purified by flash column chromatography using a mixture of acetone–petroleum ether (60:40) as eluent. Compounds **4a**–**h** were finally purified by recrystallization from hexane–toluene. The crude product containing the oily diethoxyphosphorylated amines **4i**,**j** or dimethoxyphosphorylated amines **4k**,**l** was purified by flash column chromatography using a mixture of acetone–hexanes (60:40) as eluent and the compounds **4i**,**j** and **4k**,**l** thus obtained were used directly in the next step.

Diarylenamines 3a–l; General Procedure

In an atmosphere of dry Ar, a solution of BuLi (1.6 M in hexanes, 1.25 mL, 2 mmol) or *t*-BuLi (1.7 M in pentane, 1.20 mL, 2 mmol) was added dropwise to a solution of the phosphorylated amine **4b**–**f** and **4i**–**l** (2 mmol), respectively, in THF (20 mL) at –78 °C with stirring. The orange solution was stirred for additional 15 min and a solution of the appropriate aldehyde **5a**–**f** (2 mmol) in THF (5 mL) was then slowly added. After stirring at –78 °C for 15 min the reaction mixture was allowed to come to r.t. over 1 h and further stirred for 8 h. Aq 10% NH_4Cl (10 mL) was added and the organic layer separated, rinsed with brine, dried ($MgSO_4$) and concentrated to dryness. The crude product was analyzed by ^{1}H NMR spectroscopy in order to determine the stereochemistry of the exclusively formed isomer. Enamines **3a**–**l** thus obtained were used directly in the following radical cyclization step.

Dialkyl-phenanthren-9-ylamines 2a–j; General Procedure

To a solution of crude **3a**–**l** in dry degassed toluene (250 mL), refluxing under Ar, was added a solution of Bu_3SnH (875 mg, 3 mmol) and AIBN (330 mg, 2 mmol) in anhyd degassed toluene (20 mL) dropwise over 30 min. Once the addition was finished, refluxing was kept up for a further 30 min. Benzene was evaporated under reduced pressure and the crude solid residue dissolved in MeCN (100 mL). This solution was washed with hexane (5 × 50 mL) and concentrated *in vacuo* to yield a solid residue, which was purified by flash column chromatography on silica gel using EtOAc–petroleum ether (1:1) as eluent. Solid compounds **2a**–**i** were finally recrystallized from hexane–toluene.

Alkylphenanthrene-9-ylamines 1a–j; General Procedure

A solution of compounds **2a**–**j** (3 mmol) in MeOH (25 mL) was stirred with activated Pd/C (10%, 5 mg) and HCO_2NH_4 (183 mg, 3 mmol). The mixture was refluxed for 30 min, filtered through Celite® and the solvent removed under reduced pressure. The crude residue was dissolved in CH_2Cl_2 (20 mL) and washed with water (2 × 10 mL). After drying of the organic phase ($MgSO_4$), concentration in vacuo left a solid, which was purified by chromatography on basic alumina (Merck aluminum oxide 90 active basic, 70–230 mesh ASTM) using a mixture EtOAc–petroleum ether (30:70) as eluent. Final recrystallization from pentane–toluene delivered the target aminophenanthrenes **1a**–**j**.

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