The directed *ortho* metalation – palladium catalyzed cross coupling connection. A general regiospecific route to 9-phenanthrols and phenanthrenes. Exploratory further metalation

Jian-min Fu and Victor Snieckus

Abstract: A new general and regiospecific synthesis of 9-phenanthrols (**1** + **2** → **3** → **4**, Scheme 1, Table 1) proceeding by a Directed *ortho* Metalation (DoM), Suzuki–Miyaura cross coupling, and a new LDA-mediated Directed remote Metalation sequence is described. The facile Pd-catalyzed hydrogenolysis of the phenanthrols **4** into the corresponding phenanthrenes **5** via their triflates **18** translates the original DoM regioselectivity also into a general synthesis of phenanthrenes (Table 2). Further DoM (**19** → **20, 21; 24** → **25**), cross coupling (**20c** → **23**), as well as oxidation – ring contraction (**4b, 4f** → **28a, 28b**) chemistry of phenanthrene derivatives is reported.

Key words: 9-phenanthrols, directed ortho metalation, Suzuki cross coupling, synthesis.

Résumé : On décrit une nouvelle synthèse, générale et régiospécifique, des 9-phénanthrols (**1** + **2** → **3** → **4** du tableau 1) par une séquence impliquant une réaction de métallation orientée vers la position *ortho* (DoM), un couplage croisé de Suzuki–Miyaura et une nouvelle métallation à distance orientée à l'aide de LDA. La transformation des phénanthrols (**4**) en phénanthrènes correspondants (**5**) qui se fait facilement par hydrogénolyse catalysée par le palladium des triflates (**18**) reflète la régiosélectivité de la réaction de DoM initiale en une synthèse générale des phénanthrènes (Tableau 2). On rapporte aussi d'autres réactions de DoM (**19** → **20; 21; 24** → **25**), de couplages croisés (**20c** → **23**) ainsi que la chimie de l'oxydation et de la contraction de cycle (**4b**, **4f** → **28a, 28b**) de dérivés du phénanthrène.

Mots clés : 9-phénanthrols, métallation orientée en ortho, couplage croisé de Suzuki, synthèse.

Introduction

Within the last decade, rapid and regioselective access of polysubstituted aromatics, an endeavor of special significance in the pharmaceutical industry, has been facilitated by the development of the Directed *ortho* Metalation (DoM) reaction (1). This strategy, which oftimes overcomes issues of harsh conditions and lack of regiocontrol inherent in the classical aromatic electrophilic subsitution reactions, has been extensively pursued for a variety of Directed Metalation Group (DMG) – bearing benzenes; significantly less attention has been given to exploration of DoM in more highly condensed aromatics. To take the simple step to greater complexity, naphthalene DoM chemistry has been scantily studied (2) and only sporadic reports have appeared in more highly fused aromatic systems (3). In the course of work aimed to generalize the synthetic link between DoM and the Suzuki–Miyaura Pd-catalyzed cross coupling reaction (4), the 2-carboxamido-2′-methyl biaryls **3** (Scheme 1) were prepared from partners **1** and **2** (5). At this point, stimulated by the delineation of the Complex Induced Proximity Effect (CIPE) concept (6), which was rewarded by the discovery of the LDA-mediated conversion of biaryl amides **6** into fluorenones **7** (7), we tested the conjecture that deprotonation of the vinylogously acidic 2′-methyl hydrogen in **3** would result in cyclization to 9-phenanthrols **4**, a process which, as for the conversion **6** → **7**, may be termed Directed remote Metalation (DreM).

Herein we report full details (8) of the successful verification and generalization of this reaction for the regiospecific construction of 9-phenanthrols **4**, their facile conversion into the corresponding phenanthrenes **5**, and selected further DoM, Suzuki–Miyaura cross coupling, and oxidation – ring contraction reactions of phenanthrene derivatives. Phenanthrenes

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This paper is dedicated to Professor Stephen Hanessian, our lifetime friend, in celebration of his 65th birthday and with appreciation of his lasting and purposeful contributions to chemical synthesis.

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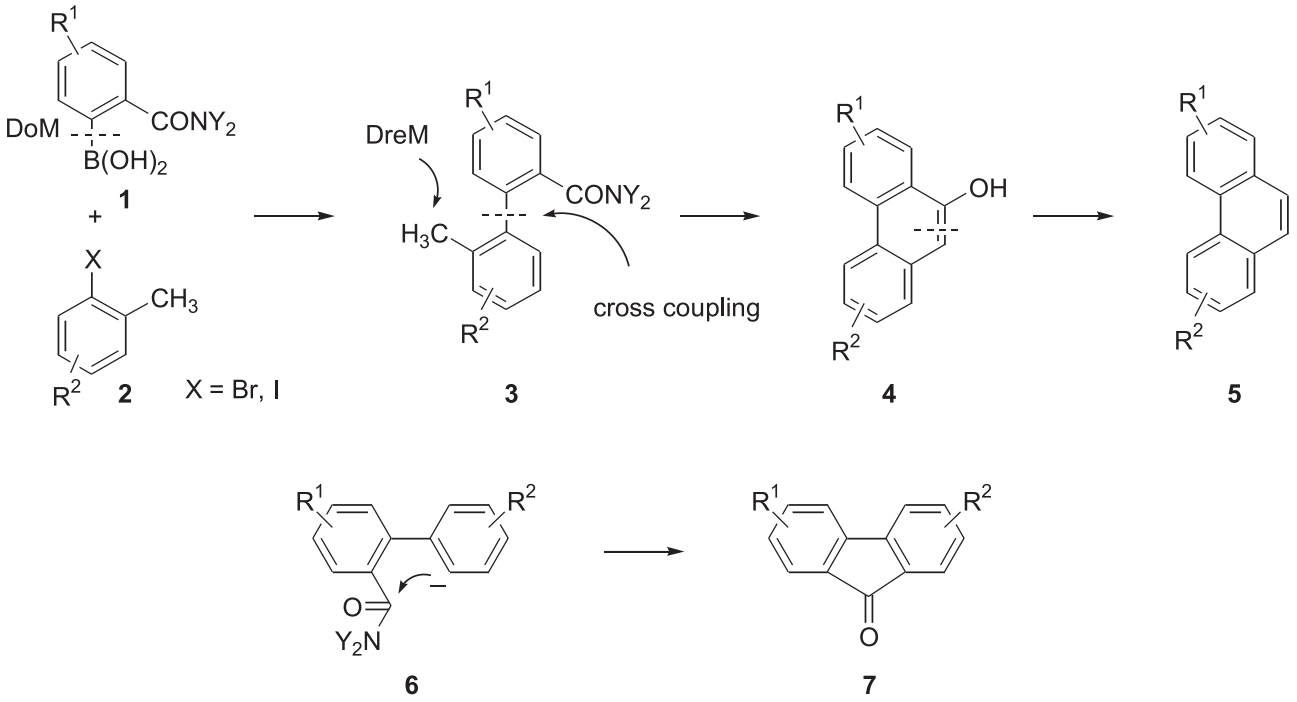
Scheme 1.



(9) represent an ambivalent class of substances which, on the one hand, are carcinogens found in the environment (10) and, on the other, natural products exhibiting potential for treatment of carcinomas and other disease states (11). Classical syntheses for phenanthrenes (12), e.g., ring annulations (13); carbocyclic ring expansion (14); intramolecular cyclization (15); and intermolecular cycloaddition (16), normally are long and laborious; inherently limited by availability of starting materials for more than trivial substitution patterns; and lack well-defined regiocontrol elements. The new carbanionic protocol (**3** → **4** → **5**) reported herein enjoys the advantages of the regiospecificity of DoM for the construction of benzamide boronic acids **1**, the ready availability of both **1** and **2** from materials of commerce, and the efficacy of the Suzuki–Miyaura reaction.

Synthesis of 2′-methylbiaryl-2-carboxamides 3 and conversion into 9-pheanthrols 4 (Table 1)

The requisite benzamide boronic acids **1** for the coupling reaction were prepared by standard *ortho*-lithiation (*s*-BuLi/TMEDA/–78°C/THF/1h) of the corresponding *N*,*N*-diethyl or *N*,*N*-diisopropyl benzamides followed by quenching with trimethyl borate and acidic workup. The boronic acids, usually obtained as fluffy solids, were not purified but directly subjected, as the excessive reactant (1.4 equiv) to the Suzuki–Miyaura cross coupling reaction (17*a*) with mainly bromo toluenes **2,** using a slightly modified procedure (DME as solvent) (17*b*, *c*). Ethanol was added as cosolvent as required for some insoluble boronic acids. Product biaryls **3** were obtained in good to excellent yields (Table 1) from coupling of unsubstituted (most entries) and methoxy (entries 3–5, 7) benzamide boronic acids **1** with 2-bromotoluenes **2** containing Cl (entries 5, 6) and electron withdrawing carboxamido (entries 8–10) and nitro (entries 11–15) groups.

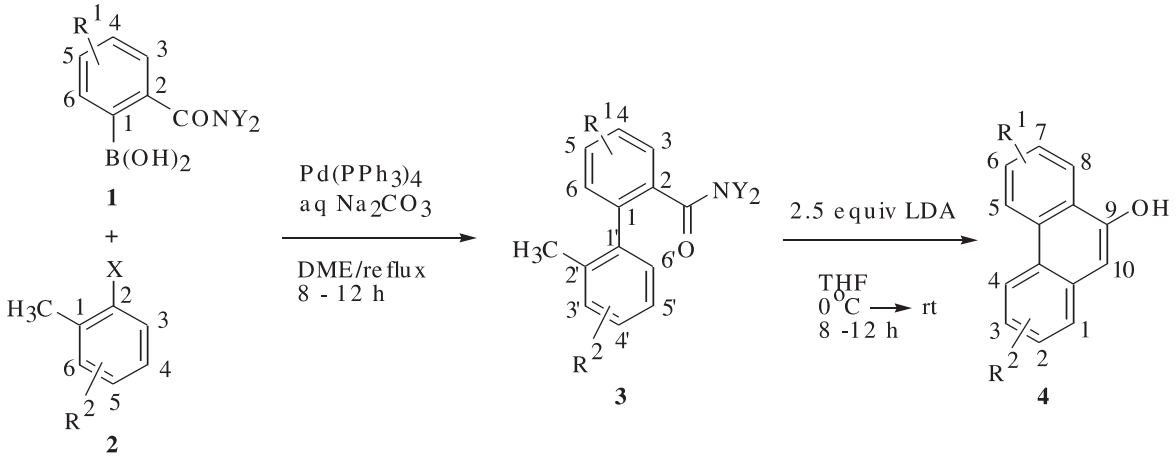
The advantage of the greater reactivity of 2-iodotoluenes and choice of solvent is evident in sterically demanding cross coupling reactions. Thus, while coupling of **1e** with 2-bromotoluene (**2a**) (Scheme 2) gave **3g** in 23% (DME) and 5% (PhH) yields respectively, the corresponding iodotoluene **2c** afforded the product **3g** in 78% yield, optimized in DME.

Consideration of pK_a data (LDA pK_a = 36 (18), 4-methylbiphenyl pK_a > 40.2 (18, 19)) and the admittedly minor vinylogous acidity effect on the methyl hydrogens in the twisted biaryl **3a** provided the expectation that equilibrium concentrations of anion **8** will be formed (Scheme 3), triggered by a CIPE from amide – LDA coordination. Subsequent cyclization to the tetrahedral intermediate **9** is ultimately driven by aromatization to **11** which could occur indirectly, via elimination to the ketone **10** or, more likely, by direct elimination. Both paths would require a second equivalent of LDA to drive the equilibrium to completion. In congruence with this hypothesis in practice, treatment of the substrate **3a** with 1 equiv. of LDA at –78°C or at 0°C followed by warming to rt overnight gave 9-phenanthrol (**4a**) in only 50–58% yield, together with recovered starting material **3a** (~40%). However, using 2.5 equiv of LDA afforded 9-phenanthrol (**4a**) in 92% isolated yield.

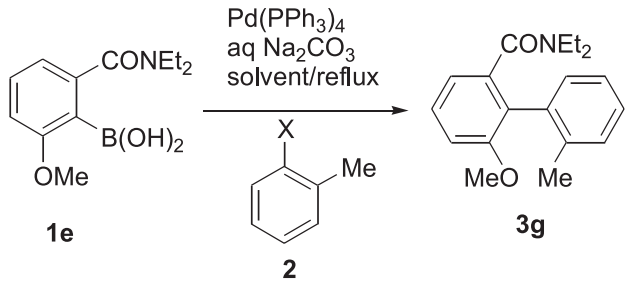
With these general conditions established, the directed remote metalation – cyclization reaction to 9-phenanthrols was then extended to other biaryl substrates (Table 1). The absence of an amide steric effect is apparent from the fact that the *N*,*N*-diisopropyl amide **3b** underwent cyclization to give 9-phenanthrol (**4a**) in comparable high yield (entry 2) to that achieved starting with the *N*,*N*-diethyl amide **3a**. Methoxy, chloro, and carboxamido substituted phenanthrols were

Table 1. Synthesis of 9-phenanthrols **4**.

	$ArB(OH)_2$ **1**			AR′X **2**			Ar – Ar′ **3**		Phenanthrols **4**			
Entry		R^1	Y		R^2	X	(Yield (%))			R^1	R^2	Yield (%)
1	**1a**	H	Et	**2a**	H	Br	**3a**	(87)	**4a**	H	H	(92)
2	**1b**	H	Pr^i	**2a**	H	Br	**3b**	(81)	**4a**	H	H	(98)
3	**1c**	3-OMe	Et	**2a**	H	Br	**3c**	(85)	**4b**	8-OMe	H	(92)
4	**1d**	5-OMe	Et	**2a**	H	Br	**3d**	(83)	**4c**	6-OMe	H	(88)
5	**1d**	5-OMe	Et	**2b**	5-Cl	Br	**3e**	(98)	**4d**	6-OMe	2-Cl	(93)
6	**1a**	H	Et	**2b**	5-Cl	Br	**3f**	(85)	**4e**	H	2-Cl	(96)
7	**1e**	6-OMe	Et	**2c**	H	I	**3g**	(78)	**4f**	5-OMe	H	(92)
8	**1a**	H	Et	**2d**	$5\text{-}CONEt_2$	Br	**3h**	(77)	**4g**	H	$2\text{-}CONEt_2$	(78)
9	**1a**	H	Et	**2e**	$4\text{-}CONEt_2$	Br	**3i**	(82)	**4h**	H	$3\text{-}CONEt_2$	(92)
10	**1b**	H	Pr^i	**2e**	$4\text{-}CONEt_2$	Br	**3j**	(79)	**4h**	H	$3\text{-}CONEt_2$	(94)
11	**1b**	H	Pr^i	**2f**	$6\text{-}NO_2$	Br	**3k**	(96)	**4i**	H	$1\text{-}NO_2$	NR
12	**1a**	H	Et	**2g**	$5\text{-}NO_2$	Br	**3l**	(82)	**4j**	H	$2\text{-}NO_2$	NR
13	**1b**	H	Pr^i	**2g**	$5\text{-}NO_2$	Br	**3m**	(98)	**4j**	H	$2\text{-}NO_2$	NR
14	**1a**	H	Et	**2h**	$4\text{-}NO_2$	Br	**3n**	(99)	**4k**	H	$3\text{-}NO_2$	NR
15	**1b**	H	Pr^i	**2h**	$4\text{-}NO_2$	Br	**3o**	(99)	**4k**	H	$3\text{-}NO_2$	NR



Scheme 2.

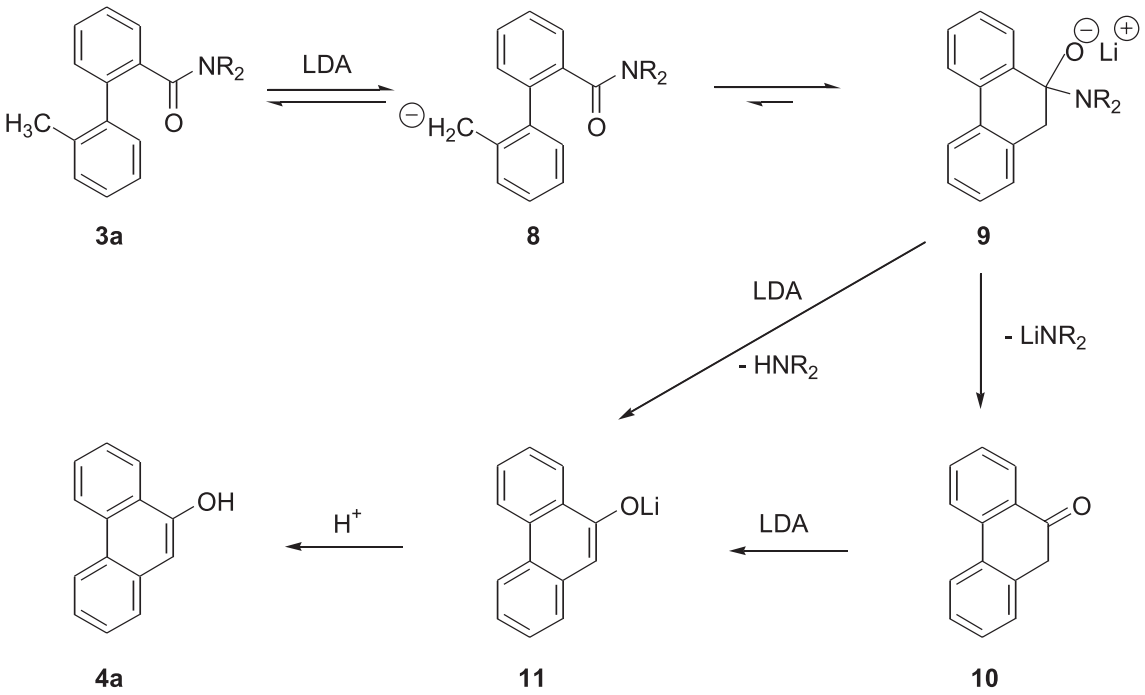


2	X	Solvent	**3g**, Yield%
2a	Br	DME	23
2a	Br	PhH	5
2c	I	PhH	29
2c	I	DME	78

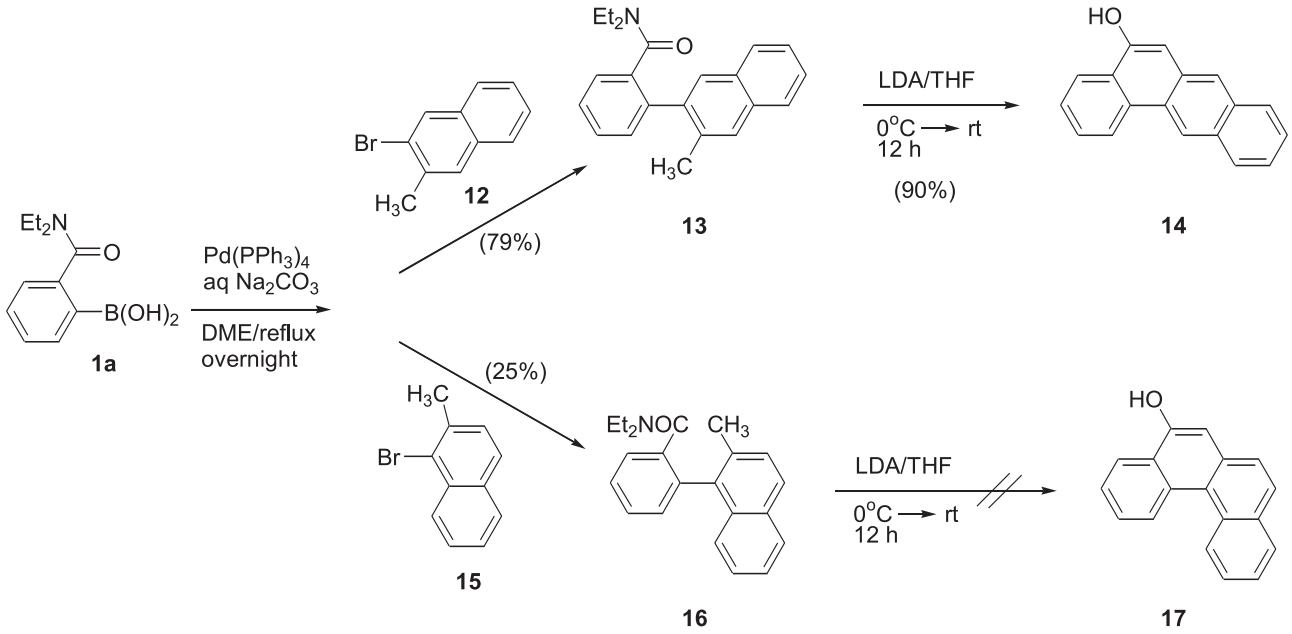
prepared in good yields (entries 3–10). The requirement of 2 equiv. of LDA for optimum yields was also ascertained in the case of 8-methoxy-9-phenanthrol (**4b**) (entry 3), formed in 92% yield compared to 63% when 1 equiv. of LDA was used. Nitro substituted biaryls failed to cyclize (entries 11–15). Although LDA addition to the THF solutions of these biaryls resulted in color changes from yellow to purple, aqueous workup led to decoloration and recovery of starting materials or decomposed products. These results may be due to the onset of single electron transfer processes between the nitrobiaryl (electron acceptor) (20) and LDA (electron donor) (21) partners. Use of bases which are successful in the Reissert indole synthesis involving 2-nitrotoluene deprotonation (e.g., NaH, KO*t*-Bu) (22) also failed to give nitro-substituted 9-phenanthrols. The characterization of some 9-phenanthrols required derivatization to acetate and (or) triflate due to their instability, as evidenced by brown discoloration after flash chromatography.

The potential value of the DreM-based 9-phenanthrol synthesis for the construction of more highly condensed polycyclic aromatics was tested on two selected cases **13** and **16** (Scheme 4) which were prepared from the cross coupling of **1a** with isomeric methyl bromonapthalenes **12** and **15** respectively. While **13** underwent LDA-mediated

Scheme 3.



Scheme 4.



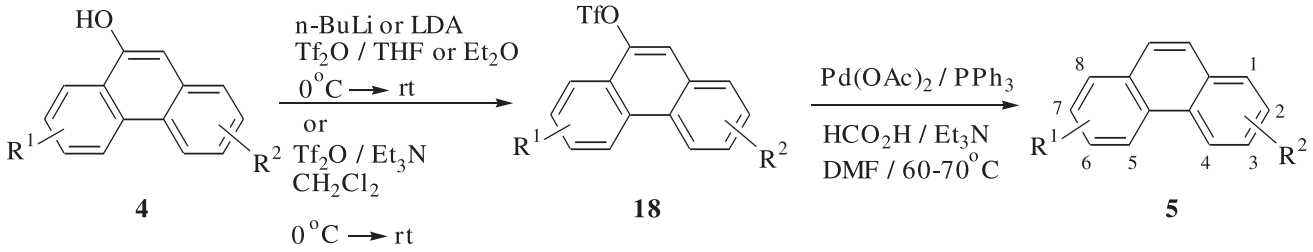
cyclization to 5-hydroxy benz[*c*]anthracene (**14**) in excellent yield, **16** failed to give the expected 10-hydroxy benz[*c*]phenanthrene (**17**) even under vigorous conditions (4 equiv of LDA in refluxing THF; quantitative recovery of **16**). The latter result, already foreshadowed by low yield in the cross coupling reaction to **16**, may be rationalized by a peri-hydrogen effect which inhibits achievement of the angle required for the non-linear (23) approach of carbanion to amide carbonyl or in the planarization needed for the tetrahedral intermediate corresponding to **9**.

The 9-phenanthrol to phenanthrene conversion (4 → 18 → 5)

To establish a general regiospecific phenanthrene synthesis based on the DreM protocol, the Pd-catalyzed hydrogenolysis of aryl triflates, independently discovered by three groups (24, 25) was adapted. Thus remarkably stable phenanthryl triflates **18** (Table 2), obtained by treatment of the corresponding phenanthrols **4** with *n*-BuLi or LDA

Table 2. Synthesis of phenanthrenes.

Entry	R^1	R^2	Triflate	Yield (%)	Phenanthrene	Yield (%)
1	H	H	**18a**	80	**5a**	67
2	8-OMe	H	**18b**	75	**5b**	97
3	6-OMe	H	**18c**	65	**5c**	73
4	H	2-Cl	**18d**	90	**5d**	68
5	5-OMe	H	**18e**	71	**5e**	93
6	H	2-$CONEt_2$	**18f**	59	**5f**	90
7	H	3-$CONEt_2$	**18g**	69	**5g**	69



followed by triflic anhydride (24*a*) or by triethyl amine – triflic anhydride, (26) were subjected to reaction with $Pd(OAc)_2$ and PPh_3 in DMF followed by addition of Et_3N and formic acid to afford phenanthrenes **5** in good to excellent yields. The overall route to phenanthrenes, **1 + 2** → **3** → **4** → **18** → **5** constitutes a general, efficient, regiospecific, and convenient process which is expected to compete favorably with known methods for the preparation of this class of aromatic hydrocarbons. For example, the phenanthrene **5b** and **5e** were obtained in 57% and 47% overall yield respectively compared to ~10% overall yield for both compounds by the Stobbe condensation involving the intramolecular cyclization reaction as the key step (27).

DoM and other reactions of 9-phenanthrols

To explore phenanthrene C_{10} – DoM paths, the *N*,*N*-diethyl 9-phenanthryl *O*-carbamate **19** (Scheme 5) was prepared from the corresponding phenanthrol (**4a**) ($ClCONEt_2$/pyridine/reflux). When subjected to the standard metalation (*s*-BuLi/TMEDA/THF/–78°C/1 h) – silylation sequence, **19** afforded product **20a** in <44% yields; however, under *t*-BuLi metalation conditions, **20a** was obtained in 88% yield. Using these conditions, the 10-methyl phenanthrene **20b** was also prepared and exclusion of electrophile allowed the anionic Fries rearrangement (28) to proceed smoothly to give compound **21** in excellent yield. Treatment of the 9-TMS phenanthrene **20a** with BBr_3 resulted in ipso borodesilylation (29) to cleanly produce the corresponding boronic acid **20c** which underwent smooth palladium catalyzed cross coupling with 4-nitrobromobenzene (**22**) to furnish the biaryl **23** in good yield (80%). This sequence of potential generality presents an alternate route to Suzuki–Miyaura cross coupling partners which allows a C-H site *ortho* to a DMG to remain in a holding pattern as the TMS masked derivative and to be subsequently exposed by an regioselective ipso process.

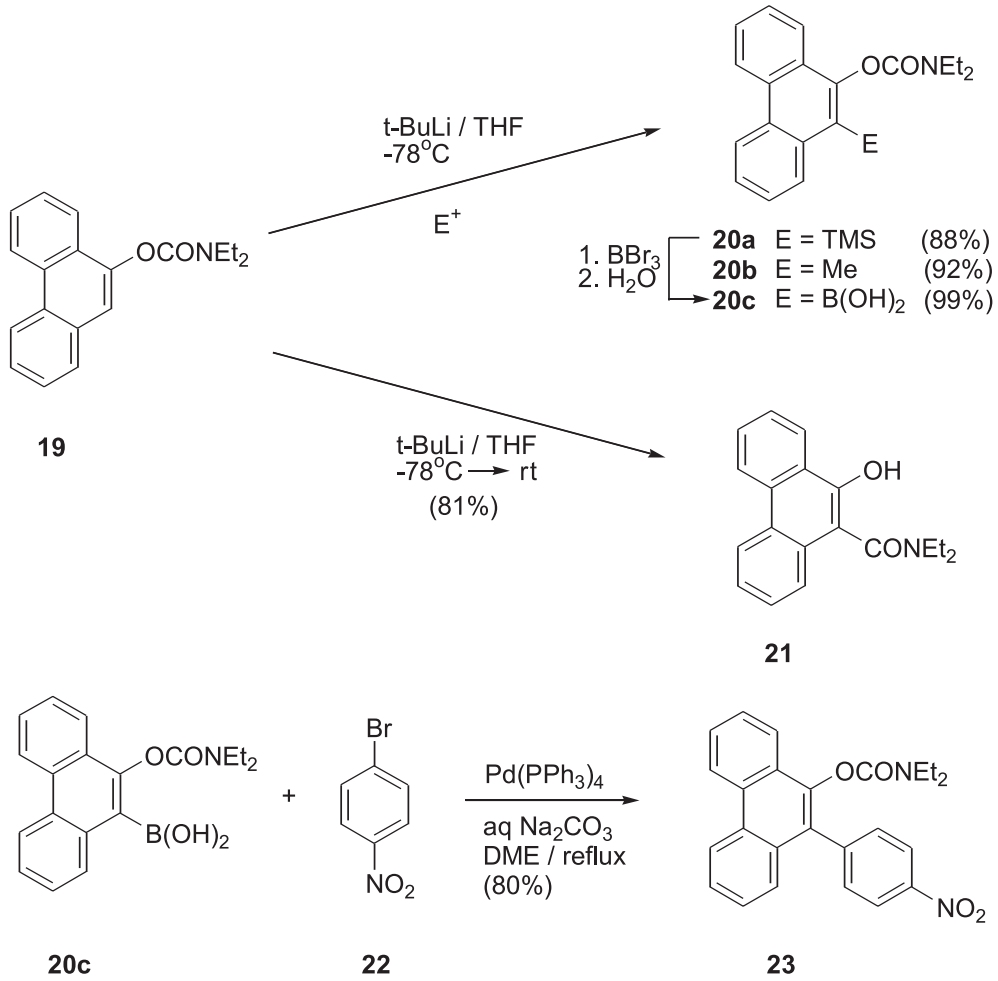
In further examination of DoM chemistry of the phenanthrene nucleus (3), the available *N*,*N*-diethyl amides **5f** and **5g** (Table 2) were subjected to the standard metalation conditions followed by quenching with TMSCl. In each case, an inseparable mixture of the TMS isomers was obtained thus rendering this reaction of limited synthetic value. On the other hand, the phenanthryl-4-*O*-carbamate **24**, prepared from 4-methoxyphenanthrene (**5e**) by demethylation with BBr_3 and carbamoylation (Scheme 6), gave, upon metalation with either *s*-BuLi and TMEDA, or *t*-BuLi in THF at –78°C and warming to rt, the anionic Fries rearrangement (28) product **25** in quantitative yield. Attempts to trap the incipient *ortho* lithiated species with electrophiles such as TMSCl led also mainly to the formation of **25** (80%), thus suggesting a rapid migration presumably resulting from steric relief of the carbamate – C_5- peri – hydrogen interaction. These restricted observations suggest that phenanthrenes are substrates for profitable DoM and cross coupling chemistry, e.g., after phenol protection in **25**, further metalation may be contemplated.

The known facile oxidation of 9-phenanthrols into 9,10-phenanthroquinones (30) and the potential for a benzil-benzilic acid rearrangement (31) in the latter invited the development of a ring-contraction route to fluorenones (32). In this pursuit, 9-phenanthrols **4b** and **4f** (Scheme 7) were oxidized by bubbling oxygen into a DMF solution containing a catalytic amount of salcomine (33) to give the methoxy phenanthroquinones **26a** and **26b** in quantitative yields. Treatment with 2 M potassium hydroxide at 90°C provided mixtures of the benzil – benzilic acid rearrangement products **27** (major) together with fluorenones **28** (minor) which, without separation, were treated with lead tetraacetate (34), to afford the fluorenones **28** in excellent overall yields. Through this simple sequence, a synthetic conduit from phenanthrene to fluorenone aromatics is established.

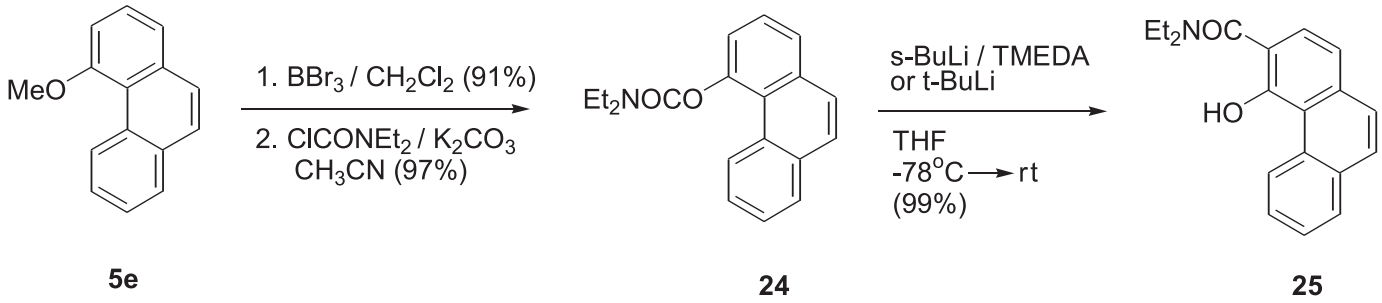
Conclusions

A new general 9-phenanthrol synthesis proceeding by a Directed *ortho* Metalation (DoM) – Suzuki–Miyaura – Directed remote Metalation (DreM) sequence (**1 + 2** → **3** → **4**, Table 1) has been demonstrated. It posits advantages of inherent regiospecificity (DoM), brevity, mild conditions, and starting material availability. Furthermore, it serves as a relay for a regioselective synthesis of the corresponding

Scheme 5.



Scheme 6.



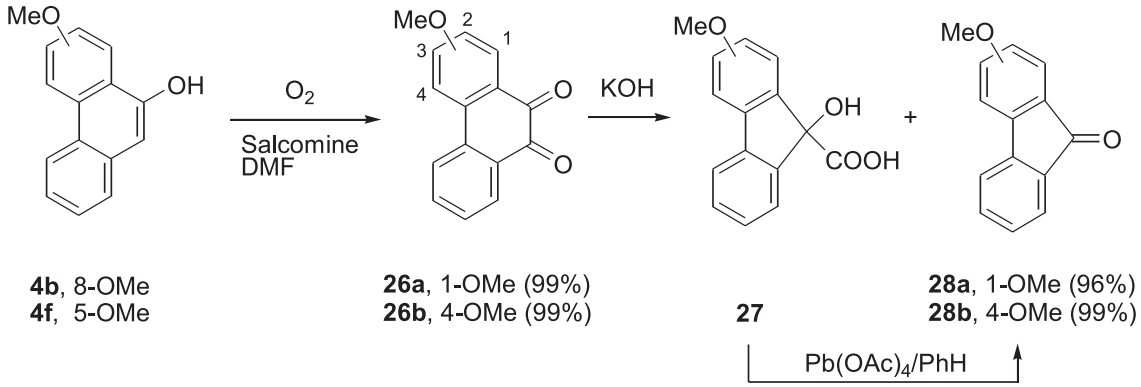
phenanthrenes by a Pd-catalyzed hydrogenolysis of the intermediate triflates (**4** → **18** → **5**, Table 2). These results together with additional exploratory DoM, cross coupling, and oxidation-rearrangement chemistry (Schemes 5–7) suggest considerable opportunity for the regiospecific construction of polysubstituted phenanthrene derivatives according to protocols elaborated herein which will compete favorably with or supercede classical methodologies.

Experimental section

General

Flash chromatography was carried out using Merck silica gel 60 (0.04–0.06 mm) purchased from BDH Chem. Co. Canada with EtOAc–hexane as eluent unless otherwise specified. Analytical thin layer chromatography (TLC) was performed using Merck precoated silica gel 60F-254 sheets. Melting points were determined using a Buchi model SMP-20 instrument and are uncorrected. IR spectra were recorded

Scheme 7.



on a Perkin-Elmer 983 IR spectrophotometer neat between NaCl plates, in $CHCl_3$ solution, Nujol, or KBr plate form. ^{1}H NMR and ^{13}C NMR spectra were recorded on AC-200 or AM-250 spectrometers in $CDCl_3$ solution using tetramethylsilane as internal standard unless otherwise specified. Mass spectra and HRMS were determined by Dr. R. Smith, McMaster University, Hamilton, Ontario, Canada, using VG 7070F or Varian spectrometers in EI mode unless otherwise specified. Elemental analysis were performed by Galbraith Laboratories, Knoxville, Tennessee. All dry solvents used were purified according to Perrin (35). Tetrahydrofuran, dimethoxyethane and diethyl ether were distilled from sodium-benzophenone ketyl under nitrogen immediately prior to use. Solutions of *n*-BuLi (hexane), *s*-BuLi (cyclohexane), and *t*-BuLi (pentane) were purchased from Aldrich Chemical Co. They were stored in resealable containers, and titrated periodically against 2,5-dimethoxybenzyl alcohol. *N*,*N*,*N′*,*N′*-Tetramethylethylenediamine (TMEDA) was dried over and distilled from CaH_2 before use. Lithium diisopropylamide (LDA) was always prepared before reactions by stirring a 1:1 mixture of diisopropylamine and *n*-BuLi at 0°C for 10 min (36). All commercial materials were purchased from Aldrich Chemical Co. or Lancaster Synthesis Ltd. Tetrakis(triphenylphosphine)palladium (0) was prepared following a literature procedure (37). All reactions were carried out under N_2 or Ar atmosphere unless otherwise specified. The –78°C temperature designated is approximate as achieved by a dry ice – acetone bath. The phrase "normal workup" means the addition of saturated aqueous NH_4Cl solution to the reaction mixture followed by CH_2Cl_2 extraction, drying over Na_2SO_4, filtration, and evaporation of the filtrate in vacuo to afford the crude product.

Synthesis of tertiary benzamides

The tertiary benzamides were prepared using the procedure described by Hall (38) from the reactions of corresponding carboxylic acids with $SOCl_2$ followed by treatment with an excess of the appropriate amines.

N,N-*Diethyl 3-methyl-4-bromobenzamide* (***2d***): bp: 120–122°C (0.02 mm). Lit. (39): bp 154°C (0.05 mm).

N,N-*Diethyl 3-bromo-4-methylbenzamide* (***2e***): mp 53–55°C (hexane); IR (KBr) 1617 cm^{-1}; ^{1}H NMR δ 1.05–1.30 (br, 6 H), 2.41 (s, 3 H), 3.20–3.60 (2 br, 4 H), 7.18–7.27 (m, 2 H), 7.54 (s, 1 H); MS *m*/*e* (rel intensity) 270 (M^+ + 2 – 1, 16), 268 (M^+ – 1, 14), 199 (34), 197 (35). Anal. calcd. for $C_{12}H_{16}BrNO$: C 53.35, H 5.97, N 5.19; found: C 53.55, H 5.96, N 5.14.

General procedure for the preparation of benzamide boronic acids (1) (method A)

A solution of the benzamide (1.00 mmol), dissolved in anhydrous THF (2 mL) was added dropwise to a stirred solution of a 1:1 *s*-BuLi–TMEDA complex or *t*-BuLi (1.10 mmol) in anhydrous THF (3 mL) at –78°C. The resulting mixture was stirred at –78°C for 1 h (unless otherwise specified), treated with an excess (4.0 mmol) of $B(OMe)_3$ and the whole was allowed to warm to room temperature overnight (8–12 h). A few drops of saturated aqueous NH_4Cl solution were added and the mixture was acidified with 2 M HCl until pH 5–6. After THF was removed in vacuo, the aqueous mixture was subjected to normal workup to afford the crude product.

*2-(*N,N-*Diethylcarboxamido)phenylboronic acid* (***1a***): According to method A, to a solution of *N*,*N*-diethyl benzamide (9.91 g, 56.74 mmol), *s*-BuLi (48.4 mL of 1.27 M solution, 61.5 mmol), and TMEDA (9.3 mL, 7.15 g, 61.5 mmol) in THF, was added $B(OMe)_3$ (25.4 mL, 23.25 g, 223.7 mmol). Acidification with 2 M HCl to pH 5–6 followed by normal workup afforded 11.63 g (94%) of **1a** as a fluffy solid which was used in cross coupling reactions without further purification.

*2-(*N,N-*Diisopropylcarboxamido)phenylboronic acid* (***1b***): According to method A, to a solution of *N*,*N*-diisopropyl benzamide (12.32 g, 60.0 mmol), *s*-BuLi (52.8 mL of 1.25 M solution, 66.0 mmol), and TMEDA (9.96 mL, 7.67 g, 66.0 mmol) in THF was added $B(OMe)_3$ (27.3 mL, 24.94 g, 240.0 mmol). Acidification with 2 M HCl to pH 5–6 followed by normal workup afforded 14.65 g (98%) of **1b** which was used in cross coupling reactions without further purification.

*3-Methoxy-2-(*N,N-*diethylcarboxamido)phenylboronic acid* (***1c***): According to method A, to a solution of *N*,*N*-diethyl 2-methoxybenzamide (6.22 g, 30.0 mmol), *s*-BuLi (25.4 mL of 1.30 M solution, 33.0 mmol), and TMEDA (5.0 mL, 3.85 g, 33.0 mmol) in THF, was added $B(OMe)_3$ (10.2 mL, 9.35 g, 90.0 mmol). Acidification with 2 M HCl to pH 5–6 followed

by normal workup afforded 7.31 g (97%) of **1c** which was used in cross coupling reactions without further purification.

*5-Methoxy-2-(*N,N-*diethylcarboxamido)phenylboronic acid (**1d**)*: According to method A, to a solution of *N*,*N*-diethyl 4-methoxybenzamide (3.40 g, 16.4 mmol), *s*-BuLi (14.0 mL of 1.29 M solution, 18.1 mmol), and TMEDA (2.7 mL, 2.01 g, 18.1 mmol) was added $B(OMe)_3$ (7.5 mL, 6.85 g, 65.7 mmol). Acidification with 2 M HCI to pH 5–6 followed by normal workup afforded 4.08 g (99%) of **1d**, which was used in cross coupling reactions without further purification.

*6-Methoxy-2-(*N,N-*diethylcarboxamido)phenylboronic acid (**1e**)*: According to method A, to a solution of *N*,*N*-diethyl 3-methoxybenzamide (2.07 g, 10.0 mmol), *s*-BuLi (8.7 mL of 1.27 M solution, 11.0 mmol), and TMEDA (1.66 mL, 1.28 g, 11.0 mmol) was added $B(OMe)_3$ (4.5 mL, 4.16 g, 40.0 mmol) at –78°C. The resulting mixture was stirred at –40°C for 4 h, quenched with saturated aqueous NH_4Cl solution at –40°C, and allowed to warm to rt over 1 h. Acidification with 2 M HCl to pH 5–6 and normal workup afforded 2.34 g (96%) of **1e** which was used in cross coupling reactions without further purification.

General procedure for the preparation of 2-methylbiaryl-2-carboxamides (3) (method B)

A mixture of $Pd(PPh_3)_4$ (0.04 mmol) and aryl halide or aryl triflate (1 mmol) in DME (3 mL) was stirred at rt for 10 min. The solution of benzamide boronic acid (**1**) (1.4 mmol) in DME (2 mL) was added. For insoluble boronic acids, a mixture of DME and a minimum amount of EtOH was used. 2 M aqueous Na_2CO_3 solution (3 mL) was added and the resulting mixture was refluxed overnight (8–12 h), cooled to rt and subjected to filtration. The filtrate was treated according to normal workup to afford the crude product.

N,N-*Diethyl 2′-methylbiphenyl-2-carboxamide (**3a**)*: According to method B, 2-bromotoluene (1.71 g, 10.0 mmol) was coupled with 2-(*N*,*N*-diethylcarboxamido)phenylboronic acid (3.01 g, 14.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.462 g, 0.40 mmol). Normal workup followed by flash chromatography (1:2) afforded 2.31 g (87%) of **3a**: mp 67–68°C (hexane), (lit. (40) bp 130–135°C (0.05 mm)); IR ($CHCl_3$) 1620 cm^{-1}; ^1H NMR δ 0.65–0.71 (t, *J* = 7.1 Hz, 3 H), 0.90 (br, 3 H), 2.20 (s, 3 H), 2.60–3.90 (m, 4 H), 7.10–7.50 (m, 8 H).

N,N-*diisopropyl 2′-methylbiphenyl-2-carboxamide (**3b**)*: According to method B, 2-bromotoluene (1.04 g, 6.12 mmol) was coupled with 2-(*N*,*N*-diisopropylcarboxamido)phenylboronic acid (2.13 g, 8.56 mmol) in the presence of $Pd(PPh_3)_4$ (0.353 g, 0.31 mmol). Normal workup followed by flash chromatography (1:2) afforded 1.46 g (81%) of **3b**: mp 93–94°C (hexane); IR ($CHCl_3$) 1618 cm^{-1}; ^1H NMR δ 0.40–0.80 (br, 3 H), 0.97–1.00 (d, *J* = 6.3 Hz, 3 H), 1.04–1.07 (d, *J* = 6.8 Hz, 3 H), 1.46–1.49 (d, *J* = 6.8 Hz, 3 H), 2.23 (s, 3 H), 3.40–3.70 (br, 2 H), 7.12–7.41 (m, 8 H); MS *m*/*e* (rel intensity) 295 (M^+, 7), 252 (17), 195 (100), 165 (25). Anal. calcd. for $C_{20}H_{25}NO$: C 81.31, H 8.53, N 4.74; found: C 80.98, H 8.61, N 4.66.

N,N-*Diethyl 3-methoxy-2′-methylbiphenyl-2-carboxamide (**3c**)*: According to method B, 2-bromotoluene (2.05 g, 12.0 mmol) was coupled with 3-methoxy-2-(*N*,*N*-diethylcarboxamido)phenylboronic acid (4.23 g, 17.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.555 g, 0.48 mmol). Normal workup followed by flash chromatography (1:1) afforded 3.02 g (85%) of **3c**: mp 90–91°C (cyclohexane); IR ($CHC1_3$) 1616 cm^{-1}; ^1H NMR δ 0.58–0.63 (t, *J* = 7.1 Hz, 3 H), 0.80–1.10 (br, 3 H), 2.20 (s, 3 H), 2.70–3.83 (m, 4 H), 3.86 (s, 3 H), 6.89–6.93 (dd, *J* = 7.6, 0.7 Hz, 1 H), 7.18–7.36 (m, 6 H); MS *m*/*e* (rel intensity) 297 (M^+, 1), 225 (100), 224 (32). Anal. calcd. for $C_{19}H_{23}NO_2$: C 76.74, H 7.80, N 4.71; found: C 76.71, H 7.84, N 4.95.

N,N-*Diethyl 5-methoxy-2′-methylbiphenyl-2-carboxamide (**3d**)*: According to method B, 2-bromotoluene (0.99 g, 5.77 mmol) was coupled with 5-methoxy-2-(*N*,*N*-diethylcarboxamido)phenylboronic acid (2.03 g, 8.08 mmol) in the presence of $Pd(PPh_3)_4$ (0.334 g, 0.29 mmol). Normal workup followed by flash chromatography (1:1) afforded 1.43 g (83%) of **3d**: bp 145–150°C (0.02 mm); IR (neat) 1637 cm^{-1}; ^1H NMR δ 0.65–0.72 (t, *J* = 7.1 Hz, 3 H), 0.86–0.93 (t, *J* = 7.0 Hz, 3 H), 2.24 (s, 3 H), 2.80–3.80 (2 br, 4 H), 3.83 (s, 3 H), 6.78–6.79 (d, *J* = 2.5 Hz, 1 H), 6.88–6.95 (m, 2 H), 7.16–7.37 (m, 4 H); MS *m*/*e* (rel intensity) EI 296 (M^+–1, 3), 225 (37), 135 (100); CI (NH_3) 299 (M^+, 20), 298 (M^++1, 100), 208 (92); HRMS (EI) calcd. for $C_{19}H_{23}NO_2$-H: 296.1652; found: 296.1649.

N,N-*Diethyl 5-methoxy-2′-methyl-4′-chlorobiphenyl-2-carboxamide (**3e**)*: According to method B, 2-bromo-5-chlorotoluene (1.22 g, 5.95 mmol) was coupled with 5-methoxy-2- (*N*,*N*-diethylcarboxamido)phenylboronic acid (2.09 g, 8.33 mmol) in the presence of $Pd(PPh_3)_4$ (0.344 g, 0.30 mmol). Normal workup followed by flash chromatography (1:3) afforded 1.94 g (98%) of **3e**: mp 95–97°C (hexane); IR ($CHC1_3$) 1628 cm^{-1}; ^1H NMR δ 0.73–0.80 (t, *J* = 7.1 Hz, 3 H), 0.90–0.97 (t, *J* = 7.1 Hz, 3 H), 2.22 (s, 3 H), 2.97–3.80 (m, 4 H), 3.83 (s, 3 H), 6.73–6.74 (d, *J* = 2.6 Hz, 1 H). 6.90–6.95 (dd, *J* = 8.5, 2.6 Hz, 1 H), 7.13–7.31 (m, 4 H); MS *m*/*e* (rel intensity) 333 (M^+, 1), 331 (M^+, 2), 261 (34), 260 (20), 259 (100). Anal. calcd. for $C_{19}H_{22}ClNO_2$: C 68.77, H 6.68, N 4.22; found: C 69.03, H 6.98, N 4.19.

N,N-*Diethyl 2′-methyl-4′-chlorobiphenyl-2-carboxamide (**3f**)*: According to method B, 2-bromo-5-chlorotoluene (1.03 g, 5.0 mmol) was coupled with 2-(*N*,*N*-diethylcarboxamido)phenylboronic acid (1.55 g, 7.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.231 g, 0.20 mmol). Normal workup followed by flash chromatography (1:1) afforded 1.28 g (85%) of **3f**: mp 83–85°C (hexane); IR ($CHC1_3$) 1615 cm^{-1}; ^1H NMR δ 0.74–0.80 (t, *J* = 7.1 Hz, 3 H), 0.94 (br, 3 H), 2.19 (s, 3 H), 2.70–3.90 (br, 4 H), 7.12–7.23 (m, 3H), 7.36–7.42 (m, 4 H); MS *m*/*e* (rel intensity) 303 (M^+, 1), 301 (M^+, 5), 231 (16), 229 (51), 166 (34), 165 (40), 58 (100). Anal. calcd. for $C_{18}H_{20}ClNO$: C 71.63, H 6.68, N 4.64; found: C 71.34, H 6.89, N 4.50.

N,N-*Diethyl 6-methoxy-2′-methylbiphenyl-2-carboxamide (**3g**)*: According to method B, 2-iodotoluene (1.73 g, 8.0 mmol) was coupled with 6-methoxy-2-(*N*,*N*-diethylcarboxamido)phenylboronic acid (2.80 g, 11.2 mmol) in the presence of

$Pd(PPh_3)_4$ (0.390 g, 0.34 mmol). Normal workup followed by flash chromatography (1:1) afforded 1.80 g (78%) of **3g**: mp 105–107°C (hexane); IR ($CHC1_3$) 1630 cm^{-1}; ^1H NMR δ 0.65–0.71 (t, *J* = 7.1 Hz, 3 H), 0.85–1.00 (br, 3 H), 2.24 (s, 3 H), 2.80–3.15 (br, 2 H), 3.80–3.85 (m, 5 H), 6.90–6.94 (dd, *J* = 8.4, 2.5 Hz, 1 H), 7.10–7.31 (m, 6 H); MS *m*/*e* (rel intensity) 297 (M^+, 11), 225 (39), 224 (28), 135 (49), 71 (100); HRMS calcd. for $C_{19}H_{23}NO_2$-H: 296.1652; found: 296.1650.

N,N-*Diethyl 2′-methyl-4′-(*N,N-*diethylcarboxamido)biphenyl-2-carboxamide (**3h**)*: According to method B, *N*,*N*-diethyl 3-methyl-4-bromobenzamide (2.07 g, 7.7 mmol) was coupled with 2-(*N*,*N*-diethylcarboxamido)phenylboronic acid (2.37 g, 10.7 mmol) in the presence of $Pd(PPh_3)_4$ (0.358 g, 0.31 mmol). Normal workup followed by flash chromatography (1:1) afforded 2.19 g (77%) of **3h**: bp 182–186°C (0.005 mm); IR (neat) 1635 cm^{-1}; ^1H NMR δ 0.70–0.76 (t, *J* = 7.1 Hz, 3 H), 0.93–1.05 (2 br, 3 H), 1.10–1.40 (2 br, 6 H), 2.23 (s, 3 H), 2.80–3.80 (m, 8 H), 7.14–7.71 (m, 7 H); MS *m*/*e* (rel intensity) 366 (M^+, 24), 294 (100), 266 (22), 221 (22), 165 (20), 100 (23); HRMS calcd. for $C_{23}H_{30}N_2O_2$: 366.2309; found: 366.2310.

N,N-*Diethyl 2′-methyl-5′-(*N,N-*diethylcarboxamido)biphenyl-2-carboxamide (**3i**)*: According to method B, *N*,*N*-diethyl 3-bromo-4-methylbenzamide (2.97 g, 11.0 mmol) was coupled with 2-(*N*,*N*-diethylcarboxamido)phenyl boronic acid (3.40 g, 15.4 mmol) in the presence of $Pd(PPh_3)_4$ (0.635 g, 0.55 mmol). Normal workup followed by flash chromatography (1:1) afforded 3.30 g (82%) of **3i**: bp 196–200°C (0. 1 mm); IR (neat) 1640, 1621 cm^{-1}; ^1H NMR δ 0.73–0.78 (t, *J* = 7.1 Hz, 3 H), 0.93–0.99 (t, *J* = 7.0 Hz, 3 H), 1.02–1.17 (br, 6 H), 2.21 (s, 3 H), 2.90–3.70 (br, 8 H), 7.21–7.47 (m, 7 H); MS *m*/*e* (rel intensity) 366 (M^+, 7), 209 (19), 193 (40), 192 (29), 121 (100), 105 (27); HRMS calcd. for $C_{23}H_{30}N_2O_2$: 366.2309; found: 366.2300.

N,N-*Diisopropyl 2′-methyl-5′-(*N,N-*diethylcarboxamido)biphenyl-2-carboxamide (**3j**)*: According to method B, *N*,*N*-diethyl 3-bromo-4-methylbenzamide (2.83 g, 10.6 mmol) was coupled with 2-(*N*,*N*-diisopropylcarboxamido)phenylboronic acid (3.65 g, 14.7 mmol) in the presence of $Pd(PPh_3)_4$ (0.611 g, 0.53 mmol). Normal workup followed by flash chromatography (1:1) afforded 3.27 g (79%) of **3j**: mp 105–107°C (hexane); IR ($CHC1_3$) 1618, 1612 cm^{-1}; ^1H NMR δ 0.60–1.19 (m, 15 H), 1.44–1.47 (d, *J* = 6.8 Hz, 3 H), 2.23 (s, 3 H), 3.20–3.80 (2 br, 4 H), 7.21–7.42 (m, 7 H); MS *m*/*e* (rel intensity) 394 (M^+, 12), 393 (20), 322 (37), 294 (16), 266 (24), 221 (100), 207 (25), 195 (21), 165 (50). Anal. calcd. for $C_{25}H_{34}N_2O_2$: C 76.10, H 8.69, N 7.10; found: C 76.23, H 8.70, N 7.08.

N,N-*Diisopropyl 2′-methyl-3′-nitrobiphenyl-2-carboxamide (**3k**)*: According to method B, 2-bromo-6-nitrotoluene (0.65 g, 3.0 mmol) was coupled with 2-(*N*,*N*-diisopropylcarboxamido)phenylboronic acid (1.05 g, 4.2 mmol) in the presence of $Pd(PPh_3)_4$ (0.139 g, 0. 12 rnmol). Normal workup followed by flash chromatography (1:1) afforded 0.98 g (96%) of **3k**: mp 97–98.5°C (hexane); IR ($CHC1_3$) 1621, 1527, 1340 cm^{-1}; ^1H NMR δ 0.59–0.62 (d, *J* = 6.7 Hz, 3 H), 0.88–1.13 (m, 6 H), 1.43–1.49 (m, 3 H), 2.36 (s, 3 H), 3.19–3.79 (m, 2 H), 7.24–7.46 (m, 6 H), 7.78–7.81 (d, *J* = 7.5 Hz, 1 H); MS *m*/*e* (rel intensity) 340 (M^+, 25), 297 (31), 240 (89), 194 (65), 165 (100). Anal. calcd. for $C_{20}H_{24}N_2O_3$: C 70.57, H 7.11, N 8.23; found: C 70.61, H 7.01, N 8.19.

N,N-*Diethyl 2′-methyl-4′-nitrobiphenyl-2-carboxamide (**3l**)*: According to method B, 2-bromo-5-nitrotoluene (1.08 g, 5.0 mmol) was coupled with 2-(*N*,*N*-diethylcarboxamido)phenylboronic acid (1.55 g, 7.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.231 g, 0.20 mmol). Normal workup followed by flash chromatography (1:1) afforded 1.27 g (82%) of **3l**: mp 94–95°C (hexane–CH_2Cl_2); IR ($CHC1_3$) 1621, 1518, 1348 cm^{-1}; ^1H NMR δ 0.73–0.78 (t, *J* = 7.1 Hz, 3 H), 0.96–1.02 (t, *J* = 7.1 Hz, 3 H), 2.31 (s, 3 H), 2.90–3.10 (br, 2 H), 3.20–3.50 (br, 2 H), 7.21–7.48 (m, 5 H), 7.99–8.04 (dd, *J* = 8.4, 2.3 Hz, 1 H), 8.12–8.13 (d, *J* = 2.3 Hz, 1 H); MS *m*/*e* (rel intensity) 312 (M^+, 11), 311 (36), 240 (56), 194 (100), 165 (96); HRMS calcd. for $C_{18}H_{20}N_2O_3$-H: 311.1397; found: 311.1393.

N,N-*Diisopropyl 2′-methyl-4′-nitrobiphenyl-2-carboxamide (**3m**)*: According to method B, 2-bromo-5-nitrotoluene (0.65 g, 3.0 mmol) was coupled with 2-(*N*,*N*-diisopropylcarboxamido)phenylboronic acid (1.05 g, 4.2 mmol) in the presence of $Pd(PPh_3)_4$ (0.139 g, 0. 12 mmol). Normal workup followed by flash chromatography (1:1) afforded 1.00 g (98%) of **3m**: mp 139–141°C (hexane–CH_2Cl_2); IR ($CHC1_3$) 1622, 1516, 1346 cm^{-1}; ^1H NMR δ 0.60–1.20 (m, 9 H), 1.45–1.48 (d, *J* = 6.6 Hz, 3 H), 2.33 (s, 3 H), 3.20–3.90 (2 br, 2 H), 7.23–7.45 (m, 5 H), 8.00–8.05 (dd, *J* = 8.4, 2.2 Hz, 1 H), 8.12–8.13 (d, *J* = 2.2 Hz, 1 H); MS *m*/*e* (rel intensity) 340 (M^+, 10), 297 (26), 240 (27), 194 (36), 165 (100). Anal. calcd. for $C_{20}H_{24}N_2O_3$: C 70.57, H 7.11, N 8.23; found: C 70.60, H 6.82, N 7.99.

N,N-*Diethyl 2′-methyl-5′-nitrobiphenyl-2-carboxamide (**3n**)*: According to method B, 2-bromo-4-nitrotoluene (1.08 g, 5.0 mmol) was coupled with 2-(*N*,*N*-diethylcarboxamido)phenylboronic acid (1.55 g, 7.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.231 g, 0.20 mmol). Normal workup followed by flash chromatography (1:2) afforded 1.55 g (99%) of **3n**: mp 124–125°C (hexane); IR ($CHC1_3$) 1618, 1517, 1348 cm^{-l}; ^1H NMR δ 0.66–0.73 (t, *J* = 7.1 Hz, 3 H), 1.03–1.10 (t, *J* = 7.1 Hz, 3 H), 2.30 (s, 3 H), 2.90–3.70 (2 br, 4 H), 7.22–7.51 (m, 5 H), 7.99 (br, 1 H), 8.07–8.13 (dd, *J* = 8.4, 2.5 Hz, 1 H); MS *m*/*e* (rel intensity) 312 (M^+, 18), 295 (61), 240 (69), 165 (100). Anal. calcd. for $C_{18}H_{20}N_2O_3$: C 69.21, H 6.45, N 8.97; found: C 68.99, H 6.36, N 8.96.

N,N-*Diisopropyl 2′-methyl-5′-nitrobiphenyl-2-carboxamide (**3o**)*: According to method B, 2-bromo-4-nitrotoluene (1.08 g, 5.0 mmol) was coupled with 2-(*N*,*N*-diisopropylcarboxamido)phenylboronic acid (1.74 g, 7.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.231 g, 0.20 mmol). Normal workup followed by flash chromatography (1:1) afforded 1.68 g (99%) of **3o**: mp 143.5–145°C (hexane–CH_2Cl_2); IR ($CHC1_3$) 1624, 1519, 1348 cm^{-1}; ^1H NMR δ 0.96–0.99 (d, *J* = 6.8 Hz, 3 H), 1.12 (br, 6 H), 1.43–1.46 (d, *J* = 6.6 Hz, 3 H), 2.32 (s, 3 H), 3.20–3.40 (br, 1 H), 3.80–4.00 (br, 1 H), 7.26–7.45 (m, 5 H), 7.95 (br, 1 H), 8.08–8.12 (dd, *J* = 8.4, 2.5 Hz, 1 H); MS *m*/*e* (rel intensity) 340 (M^+, 18), 240 (100), 165 (27). Anal. calcd. for $C_{20}H_{24}N_2O_3$: C 70.57, H 7.11, N 8.23; found: C 70.35, H 7.01, N 8.25.

General procedure for the synthesis of 9-phenanthrols (4) (method C)

To a freshly prepared solution of LDA (2.50 mmol) in THF (8 mL) at 0°C was added a solution of 2′-methylbiaryl-2-carboxamide (1.00 mmol) in THF (2 mL). The resulting mixture was stirred at rt for 3–12 h to give a brown or black solution that went colorless upon quenching with a few drops of aqueous NH_4Cl solution. This reaction mixture was acidified (2 M HCl) to pH 5–6 and the whole was evaporated to dryness in vacuo. Normal workup followed by flash chromatography afforded the desired product.

When, due to instability, 9-phenanthrol products required conversion into their acetate derivatives, these were prepared by stirring the 9-phenanthrols in acetic anhydride at rt overnight followed by evaporation to dryness in vacuo, normal workup, and flash chromatography.

*9-Phenanthrol (**4a**)*: According to method C treatment of *N,N*-diethyl 2′-methylbiphenyl-2-carboxamide (1.01 g, 4.1 mmol) with LDA (9.03 mmol) for 3 h followed by acidification, normal workup and flash chromatography (1:1) afforded 0.74 g (92%) of **4a**: mp 151–152°C (PhH) (lit. (41) mp 149–152°C); ^{1}H NMR spectrum was identical with that of authentic material (Aldrich Chem. Co.). Under similar conditions, treatment of the diisopropyl amide **3b,** (0.74 g, 2.5 mmol) with LDA (6.25 mmol) for 3 h followed by acidification, normal workup and flash chromatography (1:1) afforded 0.48 g (98%) of **4a** whose physical and spectroscopic properties were identical with those of the material obtained above.

*8-Methoxy-9-phenanthrol (**4b**)*: According to method C treatment of *N,N*-diethyl 3-methoxy-2′-methylbiphenyl-2-carboxamide (1.49 g, 5.0 mmol) with LDA (12.50 mmol) for 3 h followed by acidification, normal workup and flash chromatography (1:1) afforded 1.03 g (92%) of **4b**: mp 133–134°C (cyclohexane); IR ($CHC1_3$) 3387 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 4.08 (s, 3 H), 7.05 (s, 1 H), 7.24–7.27 (d, *J* = 7.9 Hz, 1 H), 7.39–7.46 (m, 1 H), 7.49–7.55 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1 H), 7.60–7.66 (dd, *J* = 8.2, 8.2 Hz, 1 H), 7.71–7.75 (dd, *J* = 8.0, 1.2 Hz, 1 H), 8.43–8.46 (d, *J* = 8.2 Hz, 1 H), 8.61–8.64 (d, *J* = 8.2 Hz, 1 H), 9.60 (s, 1 H); MS *m*/*e* (rel intensity) 224 (M^+, 74), 181 (100), 152 (43). Anal. calcd. for $C_{15}H_{12}O_2$: C 80.34, H 5.39; found: C 80.32, H 5.50.

*6-Methoxy-9-phenanthrol (**4c**)*: According to method C treatment of *N,N*-diethyl 5-methoxy-2′-methylbiphenyl-2-carboxamide (1.81 g, 6.1 mmol) with LDA (15.25 mmol) for 6 h followed by acidification, normal workup and flash chromatography (1:1) afforded 1.21 g (88%) of **4c** which was characterized as its *triflate* **18c** (see below).

*2-Chloro-6-methoxy-9-phenanthrol (**4d**)*: According to method C treatment of *N,N*-diethyl 5-methoxy-2′-methyl- 4′-chlorobiphenyl-2-carboxamide (0.84 g, 2.5 mmol) with LDA (6.30 mmol) for 3 h followed by acidification, normal workup and flash chromatography (1:2) afforded 0.60 g (93%) of **4d**: mp 164–167°C (hexane–CH_2Cl_2); IR ($CHC1_3$) 3333 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 3.98 (s, 3 H), 6.91 (s, 1 H), 7.25–7.30 (dd, *J* = 9.0, 2.4 Hz, 1 H), 7.35–7.39 (dd, *J* = 8.9, 2.2 Hz, 1 H), 7.80–7.81 (d, *J* = 2.2 Hz, 1 H), 8.11–8.12 (d, *J* = 2.4 Hz, 1 H), 8.15–8.18 (d, *J* = 9.0 Hz, 1 H), 8.67–8.71 (d, *J* = 8.9 Hz, 1 H), 10.46 (s, 1 H); MS m/*e* (rel intensity) 260 (M^+, 35), 258 (M^+, 100), 217 (14), 215 (41), 195 (13) which, due to instability, was converted into its *acetate*: mp 151–152°C (hexane); IR (KBr) 1747 cm^{-1}; ^{1}H NMR δ 2.48 (s, 3 H), 4.01 (s, 3 H), 7.25–7.29 (dd, *J* = 9.0, 2.3 Hz, 1 H), 7.30 (s, 1 H), 7.51–7.55 (dd, *J* = 8.9, 2.0 Hz, 1 H), 7.78–7.79 (d, *J* = 2.0 Hz, 1 H), 7.84–7.88 (d, *J* = 9.0 Hz, 1 H), 7.96–7.97 (d, *J* = 2.3 Hz, 1 H), 8.45–8.49 (d, *J* = 8.9 Hz, 1 H); MS *m*/*e* (rel intensity) 302 (M^+, 5), 300 (M^+, 16), 260 (34), 259 (17), 258 (100), 215 (31), 186 (16), 152 (26). Anal. calcd. for $C_{17}H_{l3}ClO_3$: C 67.90, H 4.36; found: C 67.97, H 4.34.

*2-Chloro-9-phenanthrol (**4e**)*: According to method C treatment of *N,N*-diethyl 2′-methyl-4′-chlorobiphenyl-2-carboxamide (0.60 g, 2.0 mmol) with LDA (5.00 mmol) for 1 h followed by acidification, normal workup and flash chromatography (1:1) afforded 0.44 g (96%) of **4e**: ^{1}H NMR (DMSO-d_6) δ 7.06 (s, 1 H), 7.40–7.44 (dd, *J* = 8.8, 2.3 Hz, 1 H), 7.62–7.75 (m, 2 H), 7.85–7.86 (d, *J* = 2.3 Hz, 1 H), 8.24–8.27 (m, 1 H), 8.66–8.70 (d, *J* = 8.8 Hz, 1 H), 8.73–8.76 (m, 1 H) which, due to instability, was converted into its *triflate* **18d** (see below).

*5-Methoxy-9-phenanthrol (**4f**)*: According to method C treatment of *N,N*-diethyl 6-methoxy-2′-methylbiphenyl-2-carboxamide (0.69 g, 2.3 mmol) with LDA (5.75 mmol) overnight followed by acidification, normal workup and flash chromatography (1:1) afforded 0.47 g (92%) of **4f** which was characterized as its *acetate*: mp 75–77°C (hexane–CH_2Cl_2); IR ($CHC1_3$) 1759 cm^{-1}; ^{1}H NMR δ 2.49 (s, 3 H), 4.14 (s, 3 H), 7.19–7.26 (m, 2 H), 7.54–7.66 (m, 4 H), 7.82–7.85 (m, 1 H), 9.62–9.65 (m, 1 H); MS *m*/*e* (rel intensity) 266 (M^+, 24), 224 (100) and its *triflate* **18e** (see below).

*2-(*N,N-*Diethylcarboxamido)-9-phenanthrol (**4g**)*: According to method C treatment of *N,N*-diethyl 2′-methyl-4′-(*N,N*-diethylcarboxamido)biphenyl-2-carboxamide (1.46 g, 4.0 mmol) with LDA (10.0 mmol) for 3 h followed by acidification, normal workup and flash chromatography (EtOAc) afforded 0.92 g (78%) of **4g**: mp 217–219°C (EtOAc); IR ($CHC1_3$) 1626 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.10–1.20 (br, 6 H), 3.20–3.70 (br, 4 H), 7.13 (s, 1 H), 7.34–7.39 (dd, *J* = 8.5, 1.6 Hz, 1 H), 7.62–7.76 (m, 3 H), 8.23–8.30 (dd, *J* = 8.1, 1.0 Hz, 1 H), 8.68–8.72 (d, *J* = 8.5 Hz, 1 H), 8.76–8.83 (m, 1 H), 10.46 (s, 1 H); MS *m*/*e* (rel intensity) 293 (M^+, 27), 221 (53); HRMS calcd. for $C_{19}H_{19}NO_2$: 293.1417; found: 293.1409.

*3-(*N,N-*Diethylcarboxamido)-9-phenanthrol (**4h**)*: According to method C treatment of *N,N*-diethyl 2′-methyl-5′- (*N,N*-diethylcarboxamido)biphenyl-2-carboxamide (3.11 g, 8.5 mmol) with LDA (21.2 mmol) for 10 min at 0°C resulted in a gray yellow turbid mixture which was quenched with saturated NH_4Cl solution at 0°C. Acidification to pH 5–6, removal of THF in vacuo, and filtration afforded 1.67 g of a **4h** as a colorless solid. Normal workup of the aqueous filtrate followed by flash chromatography (EtOAc) afforded additional product (0.63 g) for a combined yield 2.30 g (92%) of **4h**: mp 255–257°C (MeOH); IR (KBr) 3390, 1623 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.00–1.30 (br, 6 H),

3.20–3.60 (br, 4 H), 7.10 (s, 1 H), 7.43–7.47 (dd, J = 8.2, 1.3 Hz, 1 H), 7.63–7.73 (m, 2 H), 7.76–7.79 (d, J = 8.2 Hz, 1 H), 8.25–8.29 (m, 1 H), 8.59–8.60 (d, J = 1.3 Hz, 1 H), 8.78–8.82 (m, 1 H), 10.49 (s, 1 H); MS *m*/*e* (rel intensity) 293 (M^+, 40), 221 (100), 193 (20), 165 (22); HRMS calcd. for $C_{19}H_{19}NO_2$: 293.1417; found: 293.1412.

Similarly, treatment of *N*,*N*-diisopropyl 2′-methyl-5′-(*N*,*N*-diethylcarboxamido)biphenyl-2-carboxamide (0.40 g, 1.0 mmol) with LDA (2.50 mmol) for 5 min at 0°C afforded 0.276 g (94%) of **4h** whose physical and spectroscopic properties were shown to be identical with those of product obtained above.

N,N-*Diethyl 2-(3′-methylnaphthyl-2′)benzamide (**13**)*: According to method B, 2-bromo-3-methylnaphthalene (1.11 g, 5.0 mmol) was coupled with 2-(*N*,*N*-diethylcarboxamido)-phenylboronic acid (1.44 g, 6.5 mmol) in the presence of $Pd(PPh_3)_4$ (0.231 g, 0.20 mmol). Normal workup followed by flash chromatography (1:1) afforded 1.25 g (79%) of **13**: mp 85.5–87°C (hexane); IR ($CHC1_3$) 1617 cm^{-1}; ^1H NMR δ 0.44–0.51 (t, J = 7.1 Hz, 3 H), 0.7–1.1 (br, 3 H), 2.37 (s, 3 H), 2.60–3.80 (br, 4 H), 7.27–7.46 (m, 6 H), 7.69–7.78 (m, 4 H); MS *m*/*e* (rel intensity) 317 (M^+, 12), 245 (89), 244 (100), 215 (29), 202 (28). Anal. calcd. for $C_{22}H_{23}NO$: C 83.24, H 7.30, N 4.41; found: C 82.94, H 7.33, N 4.27.

*5-Hydroxy-benz[a]anthracene (**14**)*: According to method C treatment of *N*,*N*-diethyl 2-(3′-methylnaphthyl-2′)benzamide (0.461 g, 1.4 mmol) with LDA (3.64 mmol) for 3 h followed by acidification, normal workup and flash chromatography (1:1) afforded 0.32 g (90%) of **14** which was characterized as its acetate: mp 124–127°C (hexane–CH_2Cl_2) (lit. (42) mp 127–128°C); IR ($CHC1_3$) 1758 cm^{-1}; ^1H NMR δ 2.52 (s, 3 H), 7.52–7.77 (m, 5 H), 7.90–7.94 (m, 1 H), 7.99–8.14 (m, 2 H), 8.33 (s, 1 H), 8.84–8.88 (m, 1 H), 9.15 (s, 1 H); MS *m*/*e* (rel intensity) 286 (M^+, 22), 245 (20), 244 (100), 215 (48).

N,N-*Diethyl 2-(2′-methylnaphthyl-1′)benzamide (**16**)*: According to method B, 1-bromo-2-methylnaphthylene (0.88 g, 4.0 mmol) was coupled with 2-(*N*,*N*-diethylcarboxamido)phenylboronic acid (1.24 g, 5.6 mmol) in the presence of $Pd(PPh_3)_4$ (0.185 g, 0.16 mmol). Normal workup followed by flash chromatography (1:1) afforded 0.352 g (25%) of **16**: mp 137–139°C (hexane); IR (KBr) 1619 cm^{-1}; ^1H NMR δ 0.23–0.29 (t, J = 7.1 Hz, 3 H), 0.83–0.88 (t, J = 6.9 Hz, 3 H), 2.30 (s, 3 H), 2.40–3.60 (br, 4 H), 7.27–7.55 (m, 8 H), 7.72–7.80 (m, 2 H); MS *m*/*e* (rel intensity) 318 (M^++1, 49), 316 (M^+–1, 35), 246 (25), 245 (100), 244 (58), 215 (31), 202 (39). Anal. calcd. for $C_{22}H_{23}NO$: C 83.24, H 7.30, N 4.41; found: C 82.95, H 7.25, N 4.41.

General procedure for the synthesis of 9-phenanthrol triflates (18) (method D)

A solution of the 9-phenanthrol (1.0 mmol) at <0°C in Et_2O (10 mL) or THF (5 mL) was treated with *n*-BuLi or LDA (1.10 mmol), the mixture was stirred for 5 min and treated with triflic anhydride (1.1 mmol). The resulting mixture was allowed to warm to rt overnight, treated with a few drops of aqueous NH_4Cl solution and the whole was evaporated to dryness in vacuo. Normal workup followed by flash chromatography afforded the product.

*Phenanthren-9-yl trifluoromethanesulfonate (**18a**)*: According to method D, to a solution of 9-phenanthrol (1.17 g, 6.0 mmol) and *n*-BuLi (4.7 mL of 1.55 M solution, 7.2 mmol) in Et_2O at 0°C was added triflic anhydride (1.21 mL, 2.03 g, 7.2 mmol). Normal workup followed by flash chromatography (1:1) afforded 1.45 g (80%) of **18a**: bp 114–116°C (0.01 mm); IR (neat) 1412, 1211, 1135 cm^{-1}; ^1H NMR δ 7.60–7.79 (m, 5 H), 7.86–7.90 (dd, J = 7.7, 1.4 Hz, 1 H), 8.11–8.16 (m, 1 H), 8.62–8.71 (m, 2 H); MS *m*/*e* (rel intensity) 326 (M^+, 28), 193 (47), 165 (100); HRMS calcd. for $C_{15}H_9F_3O_3S$: 326.0225; found: 326.0227.

*8-Methoxyphenanthren-9-yl trifluoromethanesulfonate (**18b**)*: According to method D, to a solution of 8-methoxy- 9-phenanthrol (0.46 g, 2.1 mmol) and *n*-BuLi (1.65 mL of 1.50 M solution, 2.5 mmol) in Et_2O was added at 0°C triflic anhydride (0.42 mL, 0.70 g, 2.5 mmol). Normal workup followed by flash chromatography (1:2) afforded 0.55 g (75%) of **18b**: mp 149–151°C (hexane); IR (KBr) 1418, 1219, 1142 cm^{-1}; ^1H NMR δ 4.05 (s, 3 H), 7.13–7.16 (d, J = 8.5 Hz, 1 H), 7.56 (s, 1 H), 7.61–7.73 (m, 3 H), 7.84–7.88 (dd, J = 7.3, 1.8 Hz, 1 H), 8.32–8.35 (d, J = 8.5 Hz, 1 H), 8.62–8.65 (d, J = 8.0 Hz, 1 H); MS *m*/*e* (rel intensity), 356 (M^+, 31), 223 (29), 195 (47), 165 (100), 152 (32), 149 (27); HRMS calcd. for $C_{16}H_{11}F_3O_4S$: 356.0330; found: 356.0342.

*6-Methoxyphenanthren-9-yl trifluoromethanesulfonate (**18c**)*: According to method D, to a solution of 6-methoxy-9-phenanthrol (1.21 g, 5.4 mmol) and LDA (6.50 mmol) in THF was added triflic anhydride (1.09 mL, 1.83 g, 6.5 mmol) at 0°C. Normal workup followed by flash chromatography (1:2) afforded 1.26 g (65%) of **18c**: mp 68–70°C (hexane); IR ($CHC1_3$) 1406, 1224, 1135 cm^{-1}; ^1H NMR δ 4.04 (s, 3 H), 7.34–7.39 (dd, J = 9.0, 2.4 Hz, 1 H), 7.59 (s, 1 H), 7.61–7.74 (m, 2 H), 7.86–7.91 (m, 1 H), 8.05–8.09 (m, 2 H), 8.65–8.61 (m, 1 H); MS *m*/*e* (rel intensity) 356 (M^+, 28), 195 (100), 152 (32); HRMS calcd. for $C_{16}H_{11}F_3O_4S$: 356.0330; found: 356.0330.

*2-Chlorophenanthren-9-yl trifluoromethanesultonate (**18d**)*: According to method D, to a solution of 2-chloro-9-phenanthrol (0.457 g, 2.0 mmol) and *n*-Buli (1.63 mL of 1.55 M solution, 2.4 mmol) in THF was added at 0°C triflic anhydride (0.42 mL, 0.712 g, 2.40 mmol). Normal workup followed by flash chromatography (1:1) afforded 0.65 g (90%) of **18d**: mp 119.5–121°C (hexane); IR ($CHC1_3$) 1423, 1229, 1140 cm^{-1}; ^1H NMR δ 7.66–7.86 (m, 4 H), 7.91–7.92 (d, J = 2.2 Hz, 1 H), 8.13–8.19 (m, 1 H), 8.59–8.63 (d, J = 8.0 Hz, 1 H), 8.65–8.75 (dd, J = 8.0, 2.2 Hz, 1 H); MS *m*/*e* (rel intensity) 362 (M^+, 12), 360 (M^+, 32), 229 (17), 227 (47), 201 (34), 199 (100), 163 (26), 149 (29); HRMS calcd. for $C_{15}H_8F_3ClO_3S$: 359.9835; found: 359.9835.

*5-Methoxyphenanthren-9-yl trifluoromethanesulfonate (**18e**)*: According to method D, to a solution of 5-methoxy-9-phenanthrol (0.72 g, 3.2 mmol) and *n*-BuLi (2.36 mL of 1.50 M solution, 3.54 mmol) in THF was added triflic anhydride (0.65 mL, 1.09 g, 3.9 mmol) at –40°C. The resulting solution was warmed to –20°C, quenched with a saturated aqueous NH_4Cl solution, and the reaction mixture was allowed to warm to rt. Normal workup followed by flash chromatography (1:2) afforded 0.82 g (71%) of **18e**: mp

106–107°C (hexane); IR ($CHC1_3$) 1418, 1226, 1138 cm^{-1}; ^1H NMR δ 4.17 (s, 3 H), 7.27–7.30 (d, *J* = 7.9 Hz, 1 H). 7.60–7.83 (m, 5 H), 7.88–7.91 (dd, *J* = 7.6, 1.5 Hz, 1 H), 9.65–9.68 (d, *J* = 8.4 Hz, 1 H); MS *m*/*e* (rel intensity) 356 (M^+, 39), 223 (54), 195 (100), 152 (57); HRMS calcd. for $C_{16}H_{11}F_3O_4S$: 356.0330; found: 356.0342.

*2-(*N,N-*Diethylcarboxamido)phenanthren-9-yl trifluoromethanesulfonate (**18f**)*: To a solution of 2-(*N*,*N*-diethylcarboxamido)-9-phenanthrol (2.44 g, 8.3 mmol) and Et_3N (3.47 mL, 2.52 g, 24.9 mmol) in CH_2Cl_2 (250 mL) was added triflic anhydride (4.19 mL, 7.03 g, 24. mmol) slowly at 0°C. The resulting solution was stirred at rt overnight. Normal workup followed by flash chromatography (1:3) afforded 2.10 g (59%) of **18f**: mp 76–78°C (hexanes); IR (KBr) 1618, 1427, 1223, 1140 cm^{-1}; ^1H NMR δ 1.00–1.50 (br, 6 H), 3.20–3.80 (2 br, 4 H), 7.71–7.86 (m, 4 H), 7.94–7.95 (d, *J* = 1.7 Hz, 1 H), 8.16–8.20 (m, 1 H), 8.69–8.76 (m, 2 H); MS *m*/*e* (rel intensity) 425 (M^+, 14), 353 (30), 292 (66), 221 (31), 220 (36), 164 (36), 69 (100); HRMS calcd. for $C_{20}H_{l8}F_3NO_4S$: 425.0909; found: 425.0900.

*3-(*N,N-*diethylcarboxamido)phenanthren-9-yl trifluoromethanesulfonate (**18g**)*: To a suspension of 3-(*N*,*N*-diethylcarboxamido)-9-phenanthrol (1.47 g, 5.0 mmol) and Et_3N (2.09 mL, 1.52 g, 15.0 mmol) in CH_2Cl_2 (250 mL) at 0°C was added slowly triflic anhydride (2.52 mL, 4.23 g, 15.0 mmol). The resulting mixture was stirred and allowed to warm to rt. Normal workup followed by flash chromatography (1:1) afforded 1.46 g (69%) of **18g**: mp 89–90°C (hexanes); IR (KBr) 1629, 1413, 1215, 1137 cm^{-1}; ^1H NMR δ 1.05–1.48 (br, 6 H), 3.20–3.80 (2 br, 4 H), 7.63–7.68 (dd, *J* = 8.1, 1.5 Hz, 1 H), 7.73–7.86 (m, 3 H), 7.94–7.98 (d, *J* = 8.1 Hz, 1 H), 8.16–8.21 (m, 1 H), 8.71 (s, 1 H), 8.73–8.75 (m, 1 H); MS *m*/*e* (rel intensity) 425 (M^+, 75), 423 (41), 353 (82), 292 (69), 221 (24), 220 (100), 192 (51), 165 (32), 164 (90), 163 (48); HRMS calcd. for $C_{20}H_{l8}F_3NO_4S$: 425.0909; found: 425.0908.

General procedure for the synthesis of phenanthrenes (5) (method E):

*Phenanthrene (**5a**)*: A stirred mixture of phenanthren-9-yl trifluoromethane sulfonate (0.61 g, 2.0 mmol), $Pd(OAc)_2$ (0.018 g, 0.08 mmol), PPh_3 (0.042 g, 0.16 mmol), Et_3N (1.67 mL, 1.21 g, 12.0 mmol) and HCO_2H (0.31 mL of a 97% aqueous solution, 0.37 g, 8.00 mmol) in DMF (10 mL) was heated at 60–70°C overnight. After cooling to rt, the mixture was poured onto crushed ice (~20 mL) and the resulting solution was extracted with EtOAc (3 × 30 mL). The combined organic layer was dried (Na_2SO_4), filtered and concentrated to dryness in vacuo. Preparative TLC (hexane) afforded 0.239 g (67%) of **5a** which was shown to be identical to authentic material (Aldrich Chem. Co) by mp and spectroscopic comparison.

*1-Methoxyphenanthrene (**5b**)*: According to method E, treatment of 8-methoxy-phenanthren-9-yl trifluoromethanesulfonate (0.071 g, 0.20 mmol) with $Pd(OAc)_2$ (0.001 g, 0.004 mmol), PPh_3 (0.002 g, 0.008 mmol), Et_3N (0.084 mL, 0.06 g, 0.60 mmol) and HCO_2H (0.015 mL of a 97% aqueous solution, 0.018 g, 0.40 mmol) in DMF (1.5 mL) followed by flash chromatography (1:5) afforded 0.041 g (97%) of **5b**: mp 105–106°C (hexanes) (lit. (27) mp 105–106°C); ^1H NMR δ 4.03 (s, 3 H), 6.98–7.02 (d, *J* = 7.8 Hz, 1 H), 7.53–7.67 (m, 3 H), 7.72–7.76 (d, *J* = 9.1 Hz, 1 H), 7.87–7.91 (m, 1 H), 8.21–8.29 (m, 2 H), 8.64–8.68 (m, 1 H); MS *m*/*e* (rel intensity) 208 (M^+, 100), 193 (40), 165 (96).

*3-Methoxyphenanthrene (**5c**)*: According to method E, treatment of 6-methoxy-phenanthren-9-yl trifluoromethanesulfonate (0.178 g, 0.50 mmol) with $Pd(OAc)_2$ (0.002 g, 0.01 mmol), PPh_3 (0.005 g, 0.02 mmol), Et_3N (0.21 mL, 0.152 g, 1.50 mmol) and HCO_2H (0.04 mL of a 97% aqueous solution, 0.046 g, 1.0 mmol) in DMF (2 mL) followed by flash chromatography (hexanes) afforded 0.076 g (73%) of **5c**: mp 56–57°C (hexanes) (lit. (43) mp 57°C); ^1H NMR δ 4.03 (s, 3 H), 7.22–7.28 (dd, *J* = 8.7, 2.5 Hz, 1 H), 7.54–7.72 (m, 4 H), 7.79–7.83 (d, *J* = 8.7 Hz, 1 H), 7.85–7.90 (m, 1 H), 8.05–8.06 (d, *J* = 2.5 Hz, 1 H), 8.59–8.64 (m, 1 H); MS *m*/*e* (rel intensity) 208 (M^+, 76), 193 (19), 165 (100).

*2-Chlorophenanthrene (**5d**)*: According to method E, treatment of 2-chloro-phenanthren-9-yl trifluoromethanesulfonate (0.074 g, 0.21 mmol) with $Pd(OAc)_2$ (0.001 g, 0.004 mmol), PPh_3 (0.002 g, 0.008 mmol), Et_3N (0.09 mL, 0.062 g, 0.62 mmol) and HCO_2H (0.02 mL of a 97% aqueous solution, 0.019 g, 0.41 mmol) in DMF (2 mL) followed by preparative TLC (hexanes) afforded 0.030 g (68%) of **5d**: mp 82–83°C (lit. (44) mp 85.5–86°C); ^1H NMR δ 7.46–8.03 (m, 7 H), 8.46–8.87 (m, 2 H).

*4-Methoxyphenanthrene (**5e**)*: According to method E, treatment of 4-methoxy-phenanthren-9-yl trifluoromethanesulfonate (0.178 g, 0.50 mmol) with $Pd(OAc)_2$ (0.002 g, 0.01 mmol), PPh_3 (0.005 g, 0.02 mmol), Et_3N (0.21 mL, 0.152 g, 1.5 mmol) and HCO_2H (0.04 mL of a 97% aqueous solution, 0.046 g, 1.0 mmol) in DMF (2 mL) followed by flash chromatography (1:10) afforded 0.097 g (93%) of **5e**: mp 67–68°C (lit. (27) mp 69°C); ^1H NMR δ 4.14 (s, 3 H), 7.14–7.18 (m, 1 H), 7.50–7.76 (m, 6 H), 7.86–7.90 (dd, *J* = 7.5, 2.0 Hz, 1 H), 9.64- 9.68 (dd, *J* = 8.0, 1.4 Hz, 1 H); MS m/*e* (rel intensity) 208 (M^+, 100), 193 (35), 165 (66).

N,N-*Diethyl phenanthren-2-yl-carboxamide (**5f**)*: According to method E, treatment of 2-(*N*,*N*-diethylcarboxamido)phenanthren-9-yl trifluoromethanesulfonate (1.27 g, 3.0 mmol) with $Pd(OAc)_2$ (0.014 g, 0.06 mmol), PPh_3 (0.032 g, 0.12 mmol), Et_3N (1.25 mL, 0.911 g, 9.00 mmol) and HCO_2H (0.21 mL of a 97% aqueous solution, 0.258 g, 6.00 mmol) in DMF (15 mL) followed by flash chromatography (1:1) afforded 0.747 g (90%) of **5f**: mp 130–131°C (hexane–CH_2Cl_2); IR (KBr) 1613 cm^{-1}; ^1H NMR δ 1.23 (br, 6 H), 3.20–3.80 (2 br, 4 H), 7.58–7.82 (m, 5 H), 7.89–7.93 (m, 2 H), 8.66–8.73 (m, 2 H); MS *m*/*e* (rel intensity) 277 (M^+, 34), 276 (28), 205 (100), 177 (52), 176 (33). Anal. calcd. for $C_{19}H_{19}NO$: C 82.28, H 6.91, N, 5.05; found: C 82.13, H 6.89, N 5.04.

N,N-*Diethyl phenanthren-3-yl-carboxamide (**5g**)*: According to method E, treatment of 3-(*N*,*N*-diethylcarboxamido)phenanthren-9-yl trifluoromethane sulfonate (0.851 g, 2.00 mmol) with $Pd(OAc)_2$ (0.009 g, 0.04 mmol), PPh_3 (0.021 g, 0.08 mmol), Et_3N (0.84 mL, 0.607 g, 6.0 mmol) and HCO_2H (0.15 mL of a 97% aqueous solution, 0. 184 g, 4.00 mmol)

in DMF (10 mL) followed by flash chromatography (1:1) afforded 0.381 g (69%) of **5g**: mp 60–62°C (hexane–PhH); IR (KBr) 1604 cm^{-1}; ^1H NMR δ 1.00–1.50 (2 br, 6 H), 3.20–3.80 (2 br, 4 H), 7.58–7.81 (m, 5 H), 7.89–7.93 (m, 2 H), 8.65–8.70 (m, 2 H); MS *m*/*e* (rel intensity) 277 (M^+, 49), 276 (40), 206 (25), 205 (100), 177 (61), 176 (46), 170 (33), 152 (35); HRMS calcd. for $C_{19}H_{19}NO$: 277.1468; found: 277.1469.

N,N-*Diethyl phenanthren-9-yl*-O-*carbamate (**19**)*: A solution of 9-phenanthrol (1.94 g, 10.0 mmol) and *N*,*N*-diethylcarbamylchloride (1.77 mL, 1.90 g, 14.0 mmol) in pyridine (15 mL) was refluxed overnight, cooled, and poured onto crushed ice. The resulting solution was extracted with CH_2Cl_2 (3 x) and the organic layer was washed sequentially with saturated aqueous $NaHCO_3$ solution (2 x), aqueous HCl (2 x), brine and dried (Na_2SO_4) and filtered. The filtrate was concentrated *in vacuo* to dryness. Flash chromatography (1:2) afforded 2.50 g (85%) of **19**: mp 67–68°C (hexane–CH_2Cl_2); IR ($CHC1_3$) 1707 cm^{-1}; ^1H NMR δ 1.24–1.30 (t, *J* = 7.0 Hz, 3 H), 1.38–1.44 (t, *J* = 7.0 Hz, 3 H), 3.43–3.52 (q, *J* = 7.0 Hz, 2 H), 3.61–3.69 (q, *J* = 7.0 Hz, 2 H), 7.53–7.71 (m, 5 H), 7.82–7.85 (m, 1 H), 7.98–8.02 (m, 1 H), 8.63–8.72 (m, 2 H); MS *m*/*e* (rel intensity) 293 (M^+, 18), 165 (15), 100 (100). Anal. calcd. for $C_{19}H_{19}NO_2$: C 77.79, H 6.53, N 4.78; found: C 77.82, H 6.80, N 4.77.

N,N-*Diethyl 10-trimethylsilylphenanthren-9-yl*-O-*carbamate (**20a**)*: According to method A, to a solution of *t*-BuLi (0.75 mL of 1.60 M solution, 1.20 mmol) and *N*,*N*-diethyl phenanthren-9-yl-O-carbamate (0.29 g, 1.0 mmol) in THF (5 mL) was added TMSCl (0.51 mL, 0.44 g, 4.0 mmol). Normal workup followed by flash chromatography (1:3) afforded 0.32 g (88%) of **20a**: mp 136–137°C (hexane); IR ($CHC1_3$) 1695 cm^{-1}; ^1H NMR (CH_2Cl_2 was used as an internal standard) δ 1.25–1.30 (t, *J* = 7.1 Hz, 3 H), 1.43–1.49 (t, *J* = 7.1 Hz, 3 H), 3.35–4.00 (br, 4 H), 7.55–7.70 (m, 4 H), 7.81–7.85 (m, 1 H), 8.24–8.27 (m, 1 H), 8.67–8.74 (m, 2 H); MS *m*/*e* (rel intensity) 365 (M^+, 3), 350 (12), 250 (13), 165 (17), 100 (100). Anal. calcd. for $C_{22}H_{27}NO_2Si$: C 72.29, H 7.45, N 3.83; found: C 72.65, H 7.50, N 3.85.

N,N-*Diethyl 10-methylphenanthren-9-yl*-O-*carbamate (**20b**)*: According to method A, to a solution of *t*-BuLi **(**0.51 mL of a 1.64 M solution, 0.84 mmol) and *N*,*N*-diethyl phenanthren-9-yl-carbamate (0.21 g, 0.70 mmol) in THF (5 mL) was added iodomethane (0.18 mL, 0.40 g, 2.8 mmol). Normal workup followed by flash chromatography (1:1) afforded 0.198 g (92%) of **20b**: mp 82–84°C (hexane); IR ($CHC1_3$) 1711 cm^{-1}; ^1H NMR δ 1.25–1.30 (t, *J* = 7.1 Hz, 3 H), 1.42–1.48 (t, *J* = 7.1 Hz, 3 H), 2.58 (s, 3 H), 3.44–3.53 (q, *J* = 7.1 Hz, 2 H), 3.66–3.75 (q, *J* = 7.1 Hz, 2 H), 7.59–7.67 (m, 4 H), 7.85–7.89 (m, 1 H), 8.04–8.08 (m, 1 H), 8.65–8.71 (m, 2 H); MS *m*/*e* (rel intensity) 307 (M^+, 10), 178 (9), 100 (100); HRMS calcd. for $C_{20}H_{21}NO_2$: 307.1573; found: 307.1568.

*9-(*N,N-*Diethyl*-O-*carbamato)-phenanthren-10-yl-boronic acid (**20c**)*: To a solution of *N*,*N*-diethyl 10-trimethylsilylphenanthren-9-yl-*O*-carbamate (0.300 g, 0.82 mmol) in CH_2Cl_2 (5 mL) at –78°C was added BBr_3 (1.64 mL of 1.0 M solution in CH_2Cl_2, 1.64 mmol). The resulting mixture was stirred at rt overnight and MeOH (0.07 mL, 0.05 g, 1.64 mmol) was added. Normal workup afforded 0.273 g (99%) of **20c**, which was used without further purification in the cross coupling reaction described below.

*10-(*N,N-*Diethylcarboxamido)-9-phenanthrol (**21**)*: To a solution of *t*-BuLi (0.55 mL of a 1.70 M solution, 0.93 mmol) in THF (3 mL**)** at –78°C was added a solution of *N*,*N*-diethyl phenanthren-9-yl-O-carbamate (0.227 g, 0.77 mmol) in THF (2 mL). The reaction mixture was stirred at –78°C for 1 h and allowed to warm to rt overnight. Acidification (2 M HCl) to pH 5–6 followed by normal workup and flash chromatography (1:2) afforded 0.183 g (81%) **21**: mp 171–172°C (cyclohexane); IR ($CHC1_3$) 1598 cm^{-1}; ^1H NMR (DMSO-d_6) δ 0.82–1.34 (2 br, 6 H), 3.02–3.78 (br, 4 H), 7.48–7.62 (m, 3 H), 7.65–7.77 (m, 2 H), 8.31–8.35 (m, 1 H), 8.74–8.85 (m, 2 H), 9.78 (s, 1 H); MS *m*/*e* (rel intensity) 326 (M^+, 3), 293 (52), 221 (30), 165 (48), 164 (37), 149 (23). Anal. calcd. for $C_{19}H_{19}NO_2$: C 77.82, H 6.80, N 4.77; found: C 77.54, H 6.62, N 4.69.

N,N-*Diethyl 10-(4′-nitrophenyl)phenanthren-9-yl*-O-*carbamate (**23**)*: According to method B, 4-bromonitrobenzene (0.135 g, 0.67 mmol) was coupled with 9-(*N*,*N*-diethyl-*O*-carbamato)phenanthren-10-yl-boronic acid (0.273 g, 0.81 mmol) in the presence of $Pd(PPh_3)_4$ (0.039 g, 0.03 mmol). Normal workup followed by flash chromatography (1:5) afforded 0.219 g (80%) of **23**: mp 176–178°C (cyclohexane); IR ($CHC1_3$) 1713, 1518, 1348 cm^{-1}; ^1H NMR δ 0.95–1.07 (m, 6 H), 3.10–3.40 (br, 4 H), 7.37–7.79 (m, 7 H), 7.93–7.98 (m, 1 H), 8.34–8.39 (m, 2 H), 8.74–8.79 (d, *J* = 8.7 Hz, 2 H); MS *m*/*e* (rel intensity) 415 (25), 414 (M^+, 28), 315 (23), 268 (30), 239 (54), 100 (100); HRMS calcd. for $C_{25}H_{22}N_2O_4$: 414.1581; found: 414.1577.

N,N-*Diethyl phenanthren-4-yl*-O-*carbamate (**24**)*: To a solution of 4-methoxyphenanthrene (2.47 g, 11.8 mmol) in CH_2Cl_2 (60 mL) at –78°C was added BBr_3 (2.24 mL, 5.93 g, 23.7 mmol). The resulting mixture was stirred and allowed to warm to rt overnight. Normal workup followed by flash chromatography (1:6) afforded 2.08 g (91%) of 4-phenanthrol: mp 111–113°C (hexane) (lit. (45) mp 113–115°C); IR (KBr) 3514 cm^{-1}; ^1H NMR δ 5.71 (s, 1 H), 6.94–6.98 (dd, *J* = 7.5, 1.3 Hz, 1 H), 7.37–7.74 (m, 6 H), 7.85–7.89 (dd, *J* = 7.5, 1.9 Hz, 1 H), 9.61–9.65 (m, 1 H). A solution of the 4-phenanthrol (1.63 g, 8.4 mmol) in MeCN (50 mL) was treated with K_2CO_3 (1.62 g, 11.7 mmol) and *N*,*N*-diethylcarbamylchloride (1.49 mL, 1.59 g, 11.7 mmol) and the resulting mixture was refluxed overnight, cooled, and subjected to filtration. The filtrate was evaporated to dryness in vacuo. Normal workup followed by flash chromatography (1:5) afforded 2.39 g (97%) of **24**: mp 113–115°C (hexane); IR (KBr) 1705 cm^{-1}; ^1H NMR δ 1.23–1.29 (t, *J* = 7.1 Hz, 3 H), 1.41–1.47 (t, *J* = 7.1 Hz, 3 H), 3.43–3.52 (q, *J* = 7.1 Hz, 2 H), 3.71–3.80 (q, *J* = 7.1 Hz, 2 H), 7.31–7.34 (dd, *J* = 7.7, 1.3 Hz, 1 H), 7.53–7.61 (m, 3 H), 7.68–7.78 (m, 3 H), 7.84–7.91 (m, 1 H), 9.00–9.06 (m, 1 H); MS *m*/*e* (rel intensity) 293 (M^+, 12), 165 (13), 100 (100). Anal. calcd. for $C_{19}H_{19}NO_2$: C 77.79, H 6.53, N 4.78; found: C 77.77, H 6.53, N 4.69.

*3-(*N,N-*Diethylcarboxamido)-4-phenanthrol (**25**)*: To a yellow stirred solution of *s*-BuLi (4.01 mL of 1.15 M solution, 4.6 mmol) and TMEDA (0.70 mL, 0.54 g, 4.6 mmol) in THF (20 mL) at –78°C was added a solution of *N*,*N*-diethyl phenanthren-4-yl-*O*-carbamate (1.23 g, 4.2 mmol) in THF (5 mL). The resulting brown solution was allowed to warm to rt overnight. Normal workup followed by flash chromatography (1:1) afforded 1.22 g (99%) of **25**: oil; IR (neat) 3130 (br), 1589 cm^{-1}; ^1H NMR δ 1.30–1.36 (t, *J* = 7.1 Hz, 6 H), 3.55–3.64 (q, *J* = 7.1 Hz, 4 H), 7.33–7.37 (d, *J* = 8.3 Hz, 1 H), 7.44–7.48 (d, *J* = 8.3 Hz, 1 H), 7.56–7.72 (m, 3 H), 7.78–7.82 (d, *J* = 8.8 Hz, 1 H), 7.86–7.90 (dd, *J* = 7.7, 1.6 Hz, 1 H), 9.10 (br, 1 H), 9.81–9.84 (d, *J* = 8.7 Hz, 1 H); MS *m*/*e* (rel intensity) 293 (M^+, 59), 221 (26), 220 (100), 165 (20); HRMS calcd. for $C_{19}H_{19}NO_2$: 293.1417; found: 293.1433.

*1-Methoxy-9,10-phenanthraquinone (**26a**):* A solution of 8-methoxy-9-phenanthrol (0.173 g, 0.77 mmol) and salcomine (0.025 g, 0.077 mmol) in DMF (5 mL) at rt was subjected to a stream of O_2 via a bubbler for 4 h. The mixture was diluted with water (5 mL) and the resulting solution was extracted with EtOAc (3×). The organic layer was dried (Na_2SO_4), subjected to filtration and the filtrate was concentrated to dryness in vacuo. The resulting residue was recrystallized to afford 0.182 g (99%) of **26a**: mp 181–183°C (EtOAc); IR (KBr) 1688, 1670 cm^{-l}; ^1H NMR (DMSO-d_6) δ 3.90 (s, 3 H), 7.22–7.26 (d, *J* = 8.5 Hz, 1 H), 7.49–7.57 (ddd, *J* = 7.6, 7.5, 1.0 Hz, 1 H), 7.70–7.82 (m, 2 H), 7.86–7.90 (d, *J* = 7.9 Hz, 1 H), 7.94–7.99 (dd, *J* = 7.6, 1.5 Hz, 1 H), 8.26–8.30 (d, *J* = 8.2 Hz, 1 H); MS *m*/*e* (rel intensity) 238 (M^+, 42), 210 (46), 181 (100), 180 (30), 152 (54), 151 (25). Anal. calcd. for $C_{15}H_{10}O_3$: C 75.62, H 4.23; found: C 75.66, H 4.30.

*4-Methoxy-9,10-phenanthraquinone (**26b**)*: Following the above procedure, treatment of 5-methoxy-9-phenanthrol (0.276 g, 1.23 mmol) with O_2 in the presence of salcomine (0.04 g, 0.123 mmol) afforded 0.289 g (99%) of **26b**: mp 196–197°C (EtOAc); IR (KBr) 1689, 1661 cm^{-1}; ^1H NMR (DMSO-d_6) δ 4.01 (s, 3 H), 7.44–7.58 (m, 3 H), 7.67–7.78 (m, 2 H), 8.00–8.05 (dd, *J* = 7.7, 1.6 Hz, 1 H), 8.87–8.91 (d, *J* = 8.3 Hz, 1 H); MS *m*/*e* (rel intensity) 238 (M+, 25), 210 (79), 195 (23), 167 (28), 139 (100). Anal. calcd. for $C_{15}H_{10}O_3$: C 75.62, H 4.23; found: C 75.48, H 4.27.

*1-Methoxy-9-fluorenone (**28a**)*: A suspension of 1-methoxy-9,10-phenanthraquinone (0.165 g, 0.69 mmol) in aqueous KOH (2 M, 10 mL**)** was heated at 90°C for 1 h, cooled, and treated with conc. H_2SO_4 to pH 5–6. Normal workup gave a crude solid which was treated with $Pb(OAc)_4$ (0.841 g, 2.19 mmol) in benzene (10 mL) and the resulting mixture was stirred at rt overnight. The reaction mixture was diluted with water (10 mL), and subjected to filtration. Normal workup and flash chromatography (1:10) afforded 0.140 g (96%) of **28a**: mp 140–142°C (EtOAc) (lit. (46) mp 140–141°C); IR (nujol) 1699 cm^{-1}; ^1H NMR δ 3.98 (s, 3 H), 6.81–6.86 (d, *J* = 8.5 Hz, 1 H), 7.11–7.14 (d, *J* = 7.4 Hz, 1 H), 7.25–7.32 (ddd, *J* = 7.2, 7.2, 1.6 Hz, 1 H), 7.41–7.51 (m, 3 H), 7.63- 7.66 (dd, *J* = 7.2, 0.7 Hz); MS *m*/*e* (rel intensity) 210 (M^+, 86), 181 (100), 153 (20), 152 (44), 151 (24).

*4-Methoxy-9-fluorenone (**28b**)*: Following the above procedure, 4-methoxy-9,10-phenanthraquinone (0.098 g, 0.41 mmol) was sequentially treated with aqueous KOH (2 M, 10 mL) and $Pb(OAc)_4$ (0.549 g, 1.24 mmol) in benzene to furnish 0.086 g (99%) of **28b**: mp 114–115°C (EtOAc) (lit. (46) mp 114.5–115.5°C); IR (KBr) 1708 cm^{-1}; ^1H NMR δ 3.98 (s, 3 H), 7.03–7.06 (dd, *J* = 7.4, 1.7 Hz, 1 H), 7.19–7.31 (m, 3 H), 7.41–7.48 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 1 H), 7.61–7.64 (d, *J* = 7.3 Hz, 1 H), 7.80–7.83 (d, *J* = 7.5 Hz, 1 H); MS *m*/*e* (rel intensity) 210 (M^+, 100), 195 (21),167 (20),139 (55).

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