Regiospecific synthesis of alkylphenanthrenes using a combined directed *ortho* and remote metalation – Suzuki–Miyaura cross coupling strategy[1]

Xiongwei Cai, Stephen Brown, Peter Hodson, and Victor Snieckus

Abstract: Using a combined directed *ortho* metalation (DoM) – Suzuki–Miyaura cross coupling – directed remote metalation (DreM) approach, the alkylphenanthrenes (APs) 1-methyl- (**5a**), 1,7-dimethyl- (**5b**), 2,7-dimethyl- (**5c**), 7-ethyl-1-methyl- (**15**), and 7-*tert*-butyl-1-methylphenanthrenes (**27**) have been synthesized in four to seven steps and 21%–36% overall yields. In contrast to classical protocols, this method, which may be scaled to gram quantities, provides single isomers of APs in high purity of value as analytical standards for environmental studies. Aminocarbonylation of triflates to *N*,*N*-diethylbenzamides (**9** → **10**) and anionic Fries rearrangement (**23** → **24**) provide other potential links to DoM chemistry.

Key words: phenanthrene, directed *ortho* metalation, Suzuki–Miyaura cross coupling, synthesis, polycyclic aromatic hydrocarbon, carbonylation.

Résumé : Faisant appel à une approche combinant une métallation orientée en ortho (MOo), un couplage croisé de Suzuki et Miyaura et une métallation orientée à distance (MOdi), on a réalisé des synthèses d'alkylphénanthrènes (AP), les 1-méthyl- (**5a**), 1,7-diméthyl- (**5b**), 2,7-diméthyl- (**5c**), 7-éthyl-1-méthyl- (**15**) et 7-*tert*-butyl-1-méthylphénanthrènes (**27**), qui impliquaient de quatre à sept étapes avec des rendements globaux allant de 21 % à 36 %. Par opposition avec les protocoles classiques, cette méthode être réalisée à des échelles du gramme et elle conduit à des isomères uniques d'AP, de grande pureté qui peuvent être utilisés comme références pour des études environnementales. L'aminocarbonylation de triflates de *N*,*N*-diéthylbenzamides (**9** → **10**) et le réarrangement anionique de Fries (**23** → **24**) fournissent d'autres liens vers la chimie de la MOo.

Mots clés : phénanthrène, métallation orienté en *ortho*, couplage croisé de Suzuki et Miyaura, hydrocarbure aromatique polycyclique, carbonylation.

[Traduit par la Rédaction]

Introduction

Alkylphenanthrenes (APs) represent a significant class of polycyclic aromatic hydrocarbons (PAHs) found in soil, sediment, and other aquatic sites, which constitute environmental pollutants with substantial levels of toxicity towards marine diatoms, gastropods, mussels, crustaceans, and especially fish (1–3). The key biological marker for toxicity, retene (7-isopropyl-1-methylphenanthrene) causes reductions in recruitment and growth and an increased prevalence of morphological abnormalities of laval pink salmon and Pacific herring (3, 4), effects which were observed in the 1989 Exxon Valdez oil spill in Alaska (1). Among the various PAH classes, the APs have been sparsely evaluated for toxicity effects, arguably because of lack of commercial sources of analytically pure compounds in sufficient quantity. Only a few APs are available, e.g., 1-methyl-, 1,7-dimethylphenanthrene, and retene at times of uncertain and insufficient isomer purity and inadequate quantity.[3] Among the few methods of phenanthrene synthesis, classical electrophilic substitution (5), Pschorr reaction (6), ring expansion (7), Mallory photocyclization (8), and recently, palladium-catalyzed trimerization (9) and radical cyclization (10), tactics have, to various degrees, been applied to AP preparation but suffer in length or produce mixtures of isomers. We report a combined metalation – Suzuki–Miyaura cross cou-

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This manuscript is dedicated to Ed Piers for placing Canadian synthetic organic chemistry on the international map.

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[3]1,7-Dimethylphenanthrene and retene available from Chiron AS, Stiklestadveien 1, Trondheim, N-7041, Norway; 1-methylphenanthrene available from Absolute Standards, Inc., Hamdan, Conn. 06518, U.S.A.

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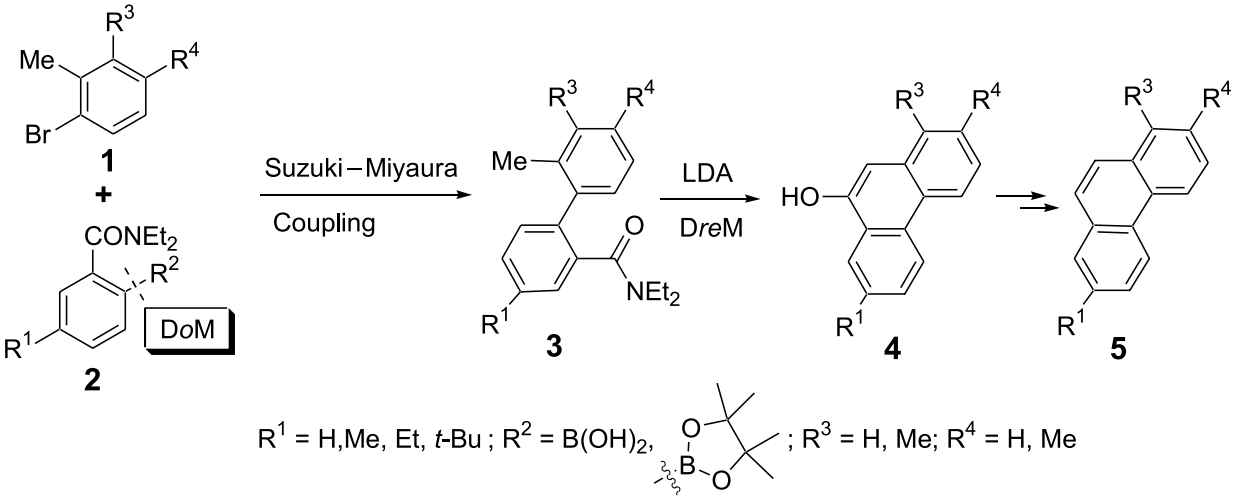
Scheme 1.



pling methodology involving both directed *ortho* (DoM) and remote metalation (DreM) reactions, **1** + **2** → **3** → **4** → **5** (Scheme 1) that provides short, efficient, and regioselective routes to APs **5a**, **5c**, **15**, and **27**. This general strategy provides the phenanthrene class of PAHs as single isomers in preparative quantities and contrasts with classical methods, which invariably involve harsh conditions, lack of regioselectivity, and considerable handling of potentially toxic materials (11). Recently, de Koning et al. has reported a general phenanthrene synthesis using *t*-BuOK-mediated cyclization of esters corresponding to **3** (12).

Synthesis of 1-methyl- (5a), 1,7-dimethyl- (5b), and 2,7-dimethyl- (5c) phenanthrenes

The synthesis of 1-methylphenanthrene (**5a**) (Scheme 2) was initiated from *N*,*N*-diethylbenzamide (**6a**) that upon metalation under standard conditions (*s*-BuLi / TMEDA / –78 °C / THF / 1 h) followed by quenching with trimethyl borate and acidic workup afforded the boronic acid **2a**. Without purification, **2a** was subjected, as the reactant in excess (1.4 equiv.), to the Suzuki–Miyaura cross coupling reaction with the commercially available 3-bromo-*o*-xylene to give the biaryl amide **3a** in good yield. Metalation–boronation of **6b**, the insecticide DEET® (13), at –98 °C proceeded smoothly to give the corresponding boronic acid, which was isolated and purified as the pinacol boronate **2b**. NMR analysis provided structural confirmation that DoM of **6b** occurred exclusively on C-6, a result differing with Beak and Brown's observation that metalation of **6b** under similar conditions but using MeOD quench yields C-6 and C-2 deuterated products in the ratio of 2:1 (Scheme 2) (14). The observed difference in regioselectivity using trimethyl borate as the electrophile may be due to its greater size. Boronate **2b** was subjected to Suzuki–Miyaura cross coupling with 3-bromo-*o*-xylene and 4-bromo-*m*-xylene to give biaryls **3b** and **3c**, respectively, in satisfactory yields.

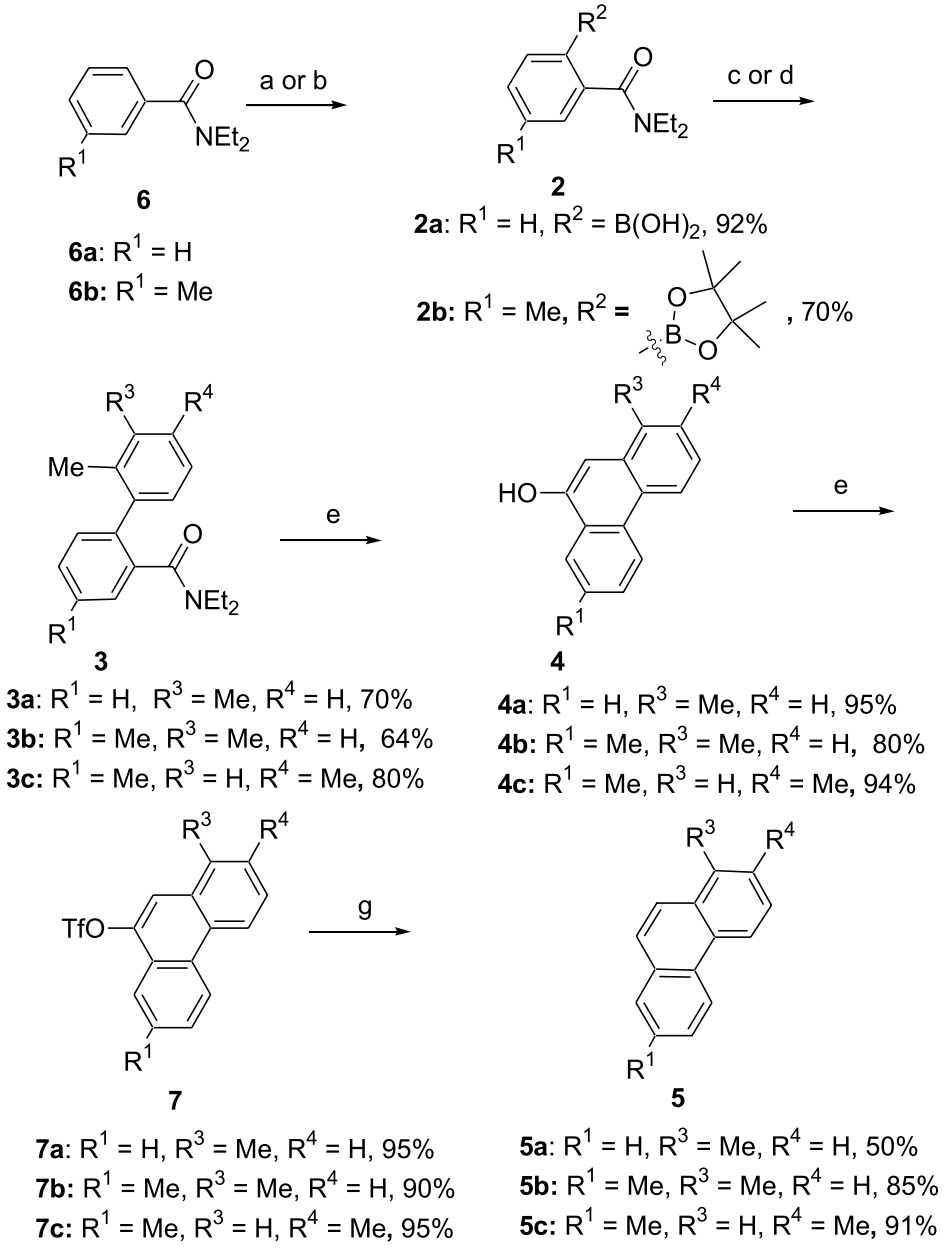
Application of the standard DreM conditions (11*a*) to the biaryl amides **3a**–**3c** (2.5 equiv. of LDA / THF / 0 °C) resulted in smooth cyclization to the 9-phenanthrols **4a**–**4c**, which underwent oxidation slowly and changed colors in the air but were stable in sealed vials at –30 °C. The 9-phenanthrols **4a**–**4c** were then converted into their triflates **7a**–**7c** (15), which upon Pd-catalyzed hydrogenolysis in the presence of formic acid, afforded 1-methyl-phenanthrene (**5a**), 1,7-dimethylphenanthrene (**5b**), and 2,7-dimethylphenanthrene (**5c**) in modest to excellent yields. Overall yields (**5a** (29%), **5b** (27%), **5c** (45%), in four to six steps from commercial materials) cannot be compared with previous routes for lack of data with the exception of **6a**, which was obtained by Pschorr synthesis in 21% overall yield and four steps (16).

Synthesis of 7-ethyl-1-methylphenanthrene (15)

The synthesis of the homologous 7-ethyl-1-methylphanthrene (**15**) commenced from 3-ethylbenzamide (**10**), which was obtained by a aminocarbonylation protocol (Scheme 3). Thus, commercial 3-ethylphenol (**8**) was converted into the corresponding triflate **9** (15), which was subjected to aminocarbonylation conditions (17) using a number of phosphine ligands that included PPh_3, dppf, and dppp. In the case of PPh_3, rapid black precipitation was observed and the product **10** was obtained in low yield with the material balance being recovered starting material (72%). In contrast, the bidentate ligands dppp and dppf behaved well, leading to similar yields of **10** and completion of reactions with only trace amounts of starting material being detected by GC at the conclusion of the reaction. In this two-phase reaction, it is imperative to ensure good mixing, especially when the reaction is carried out on a large scale. Thus, using a balloon of CO led to poorer yields and longer completion times compared to bubbling CO into the solution for the duration of the reaction.

Metalation of 3-ethylbenzamide **10** (Scheme 4) under the low-temperature conditions used previously for **6b** (Scheme 2) followed by boronation and treatment with pinacol paralleled the reaction of **6b** in that it led to the formation of boronate **11**, the product of exclusive C-6 deprotonation. The isolated and purified boronate **11** was subjected to Suzuki–Miyaura cross coupling with 3-bromo-*o*-xylene under the previously defined conditions to afford the biaryl amide **12**, which, upon treatment with LDA, led cleanly to the 9-phenanthrol **13**. Analogous to the **4** → **7** reactions,

Scheme 2. Reagents and conditions: (*a*) (*i*) *s*-BuLi / TMEDA / THF / –78 °C; (*ii*) $B(OMe)_3$ / –78 °C; (*iii*) aq. NH_4Cl; (*b*) (*i*) *s*-BuLi / TMEDA / THF / –98 °C; (*ii*) $B(OMe)_3$ / –98 °C; (*iii*) aq. NH_4Cl; (*iv*) pinacol / $MgSO_4$ / CH_2Cl_2/ 0 °C; (*c*) $Pd(PPh_3)_4$ / DME / Na_2CO_3 / 6-bromo-*o*-xylene / reflux / 4 h; (*d*) $Pd(PPh_3)_4$ / DME / Na_2CO_3 / 6-bromo-*m*-xylene / reflux/ 4 h; (*e*) (*i*) LDA / THF / 0 °C; (*ii*) aq. NH_4Cl; (*f*) 2,6-lutidine / Tf_2O / CH_2Cl_2 / 30 min; (*g*) $Pd(OAc)_2$ / PPh_3 / Et_3N / HCO_2H / DMF / 60 °C / 20 min.



6

6a: R^1 = H
6b: R^1 = Me

2

2a: R^1 = H, R^2 = $B(OH)_2$, 92%
2b: R^1 = Me, R^2 = , 70%

3

3a: R^1 = H, R^3 = Me, R^4 = H, 70%
3b: R^1 = Me, R^3 = Me, R^4 = H, 64%
3c: R^1 = Me, R^3 = H, R^4 = Me, 80%

4

4a: R^1 = H, R^3 = Me, R^4 = H, 95%
4b: R^1 = Me, R^3 = Me, R^4 = H, 80%
4c: R^1 = Me, R^3 = H, R^4 = Me, 94%

7

7a: R^1 = H, R^3 = Me, R^4 = H, 95%
7b: R^1 = Me, R^3 = Me, R^4 = H, 90%
7c: R^1 = Me, R^3 = H, R^4 = Me, 95%

5

5a: R^1 = H, R^3 = Me, R^4 = H, 50%
5b: R^1 = Me, R^3 = Me, R^4 = H, 85%
5c: R^1 = Me, R^3 = H, R^4 = Me, 91%

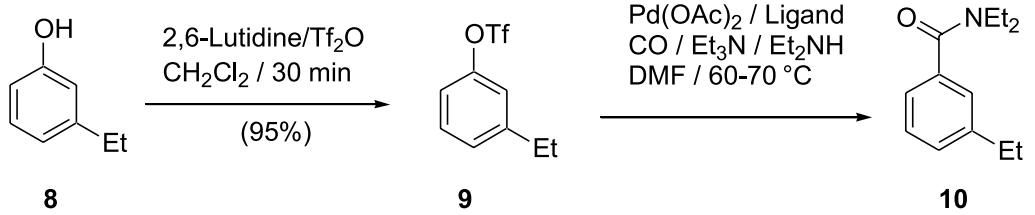
conversion of **13** into its triflate **14** followed by Pd-catalyzed hydrogenolysis by the agency of formic acid furnished **15** in high yield and >98% purity (HPLC analysis). This concluded the synthesis of 7-ethyl-1-methylphenthrene (**15**) in six steps in an overall yield of 36%.

Synthesis of 7-*tert*-butyl-1-methylphenanthrene (27)

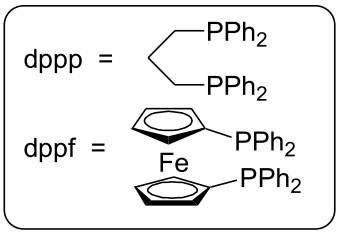
In pursuit of the same strategy (Scheme 3) for the synthesis of 7-*tert*-butyl-1-methyl-phenanthrene (**27**, Scheme 5), we envisaged the preparation of the requisite benzamide **18** by the amidocarbonylation of **17**, which, in turn, was available in high yield from the commercial phenol **16** (Scheme 6). However, modest exploration of conditions and bidentate phosphine ligands for the reaction **17** → **18**, as indicated in tabular form, gave unsatisfactory results.

Therefore, a strategy involving the inversion of coupling partners in the Suzuki–Miyaura reaction **20** + **21** → **19** was pursued (Scheme 7). Thus, 4-*tert*-butylphenol **22** (Scheme 5) was quantitatively converted into the *O*-carbamate **23** that was subjected to conditions (*s*-BuLi / TMEDA / –78 °C) for the anionic Fries rearrangement (18) to give the salicylamide **24** in good yield. Conversion of **24** into triflate **20** using 2,6-lutidine proceeded in low yield (20%) compared to that achieved for previously prepared triflates. However, using pyridine as catalyst, **20** was obtained in good yield. In the key step, triflate **20** underwent Suzuki–Miyaura cross cou-

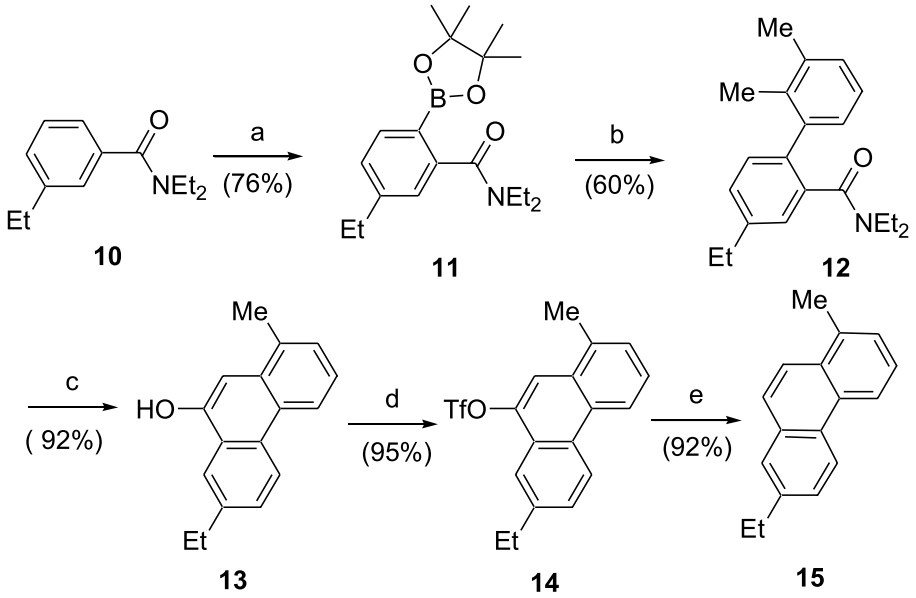
Scheme 3.



Ligand	Time (h)	Yld (%)
PPh_3	24	25
dppp	4	70
dppf	12	62



Scheme 4. Reagents and conditions: (*a*) (*i*) *s*-BuLi / TMEDA / THF / –98 °C; (*ii*) $B(OMe)_3$ / –98 °C, (*iii*) aq. NH_4Cl; (*iv*) pinacol / $MgSO_4$ / CH_2Cl_2 / 0 °C; (*b*) $Pd(PPh_3)_4$ / DME / Na_2CO_3 / 6-bromo-*o*-xylene / reflux / 4 h; (*c*) (*i*) LDA / THF / 0 °C; (*ii*) aq. NH_4Cl; (*d*) 2,6-lutidine / Tf_2O / CH_2Cl_2 / 30 min; (*e*) $Pd(OAc)_2$ / PPh_3 / Et_3N / HCO_2H / DMF / 60 °C / 20 min.



pling with the commercial boronic acid **21**, to form the biaryl amide **19** in very good yield. As before, LDA-mediated cyclization furnished, in excellent yield, the 9-phenanthrol **25** that was converted into its triflate **26** and thence into the target 7-*tert*-butyl-1-methylphenanthrene **27**. Thus, the synthesis of **27** was accomplished in seven steps in an overall yield of 21%.

Conclusion

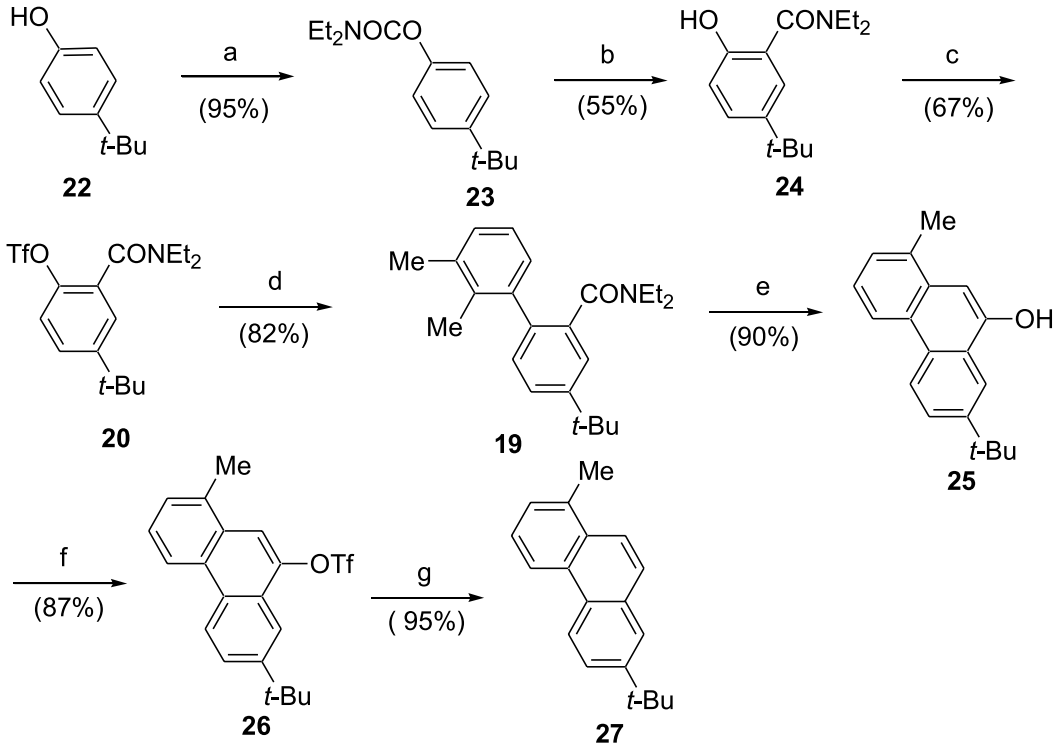
This work constitutes a contribution for the convenient and efficient preparation of the phenanthrene class of PAHs that contrasts with classical methods in terms of regioselectivity, brevity, mildness of conditions, and necessity for considerable handling of potentially toxic materials. Thus, the alkylphenanthrenes (APs) 1-methyl- (**5a**), 1,7-dimethyl- (**5b**), 2,7-dimethyl- (**5c**), 7-ethyl-1-methyl- (**15**), and 7-*tert*-butyl-1-methyl (**27**) phenanthrenes have been synthesized by a combined D*o*M – Suzuki–Miyaura cross coupling – DreM methodology in overall yields of 29% (five steps), 27% (five steps), 45% (five steps), 36% (six steps), and 21% (seven steps), respectively. A general and effective methodology has been thereby provided that allows anticipated application for the synthesis of various APs as single isomers in high purity and in scales ranging from 1 to 4 g. As an adjunct, a representative aminocarbonylation method of readily available aryl triflates to *N*,*N*-diethylbenzamides has been briefly investigated (Scheme 3) based on which a further general link to D*o*M chemistry may be anticipated.

Experimental section

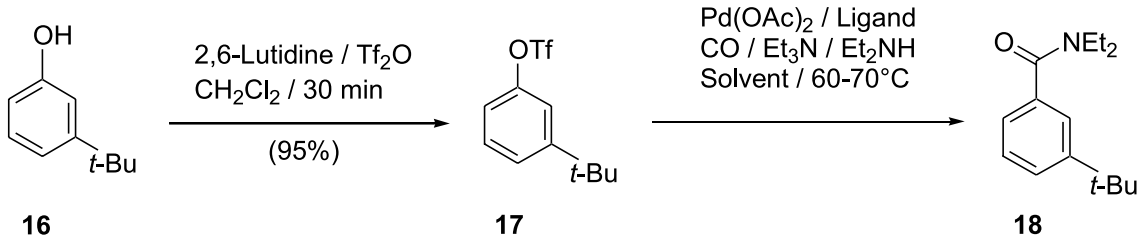
General methods

Melting points are uncorrected. IR spectra were recorded neat or as KBr discs using a BOMEM FT-IR spectrometer.

Scheme 5. Reagents and conditions: (*a*) (*i*) NaH / THF / 0 °C; (*ii*) $ClCONEt_2$; (*b*) (*i*) *s*-BuLi / TMEDA / THF / –78 °C to rt; (*ii*) aq. NH_4Cl; (*c*) Tf_2O / pyridine / CH_2Cl_2; (*d*) $Pd(PPh_3)_4$ / DME, Na_2CO_3 / **21** / reflux / 4 h; (*e*) LDA / THF / 0 °C; (*ii*) aq NH_4Cl; (*f*) 2,6-lutidine / Tf_2O / CH_2Cl_2 / 30 min; (*g*) $Pd(OAc)_2$ / PPh_3 / Et_3N / HCO_2H / DMF / 60 °C / 20 min.

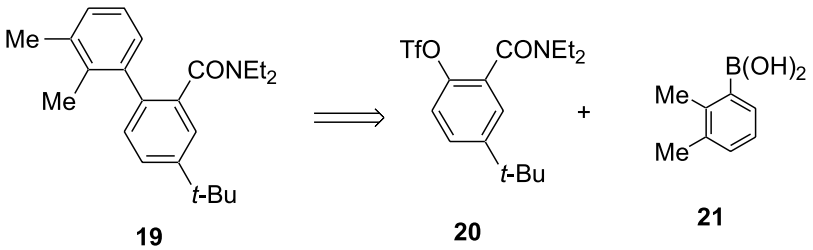


Scheme 6.



Ligand	Solvent	Time (h)	Yld (%)
dppp	DMF	24	20
dppf	DMF	24	22
dppp	DMSO	48	25
dppf	DMSO	48	27

Scheme 7.



^{1}H (300 MHz) and ^{13}C (75.43 MHz) NMR spectra were obtained in $CDCl_3$ using either TMS (for ^{1}H) or $CDCl_3$ (for ^{13}C) as the internal standard on a Bruker Avance-300 spectrometer. THF was freshly distilled from sodium benzophenone ketyl under nitrogen and CH_2Cl_2 and HN-*i*-Pr_2 were freshly distilled from CaH_2 under nitrogen. *n*-Butyllithium and *s*-butyllithium were purchased from Aldrich as solutions in hexanes, stored in resealable containers, and titrated periodically against *s*-butanol using 1,10-phenanthroline as the indicator (19). *N*,*N*-Diethyl benzamide (**6a**) was prepared from benzoyl chloride (20). *N*,*N*-Diethyl toluamide (DEET®) (**6b**), 6-bromo-*o*-xylene, 6-bromo-*m*-xylene, and 2,3-dimethylphenylboronic acid (**21**) were purchased from Aldrich Chemical Co. All experiments were carried out under argon in dried glassware, using syringe-septum cap techniques. The –78 °C and 0 °C external bath temperatures designated are approximate as achieved by a dry ice–acetone or ice–salt baths, respectively. Flash column chromatography was carried out using Merck Kieselgel 60 silica gel (particle size 32–63) with different ratios of EtOAc–hexane as eluents.

General procedures

A. Lithiation of benzamides

A solution of the benzamide (1.00 mmol) in anhyd THF (2 mL) was added dropwise to a stirred solution of *s*-BuLi–TMEDA (1:1, 1.20 mmol) complex in anhyd THF (3 mL) at –78 °C. The resulting mixture was stirred at –78 °C for 1 h, treated with an excess of $B(OMe)_3$ (2.40 mmol), and the mixture was warmed to ambient temperature over 8–12 h and quenched with a satd. aq. NH_4Cl solution (5 mL). The aqueous portion was extracted with Et_2O (3 × 5 mL), and the extract was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash column chromatography (EtOAc–hexanes) to afford the product.

B. Cross coupling reaction of arylboronic acids with aryl halides and aryl triflates

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 room temperature (rt) for 10 min. The solution of aryl boronic acid (1.4 mmol) in a minimum amount of ethanol (1 mL) and DME (2 mL) mixture was added, followed by the addition of 2 mol L^{-1} aq. Na_2CO_3 solution (3 mL). The resulting mixture was heated at reflux for 12 h, cooled to rt, and extracted with Et_2O (3 × 5 mL). The organic extract was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash column chromatography (EtOAc–hexanes) to afford the product.

C. Synthesis of 9-phenanthrols

To a solution of LDA (2.50 mmol) in THF (8 mL) was added a solution of 2′-methyldiphenyl-2-carboxamide (1.00 mmol) in THF (2 mL) at 0 °C. The resulting mixture was stirred at rt for 30 min and quenched with a satd. aq. NH_4Cl solution (5 mL). The aqueous portion was extracted with Et_2O (3 × 5 mL) and the extract was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash column chromatography (EtOAc–hexanes) to afford the product.

D. Synthesis of triflates

A solution of the phenanthrol (1.00 mmol) and 2,6-lutidine or pyridine (1.2 mmol) in CH_2Cl_2 (10 mL) was stirred for 5 min at 0 °C followed by the addition of triflic anhydride (1.20 mmol). The resulting mixture was stirred at rt for 30 min and water was added (5 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (3 × 10 mL). The combined extract was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash column chromatography (EtOAc–hexane) to afford the product.

2-(N,N-Diethylcarboxamido)phenylboronic acid (2a)

According to general procedure A, a solution of *N*,*N*-diethylbenzamide (1.77 g, 10.0 mmol), *s*-BuLi (9.60 mL of a 1.25 mol L^{-1} solution, 12.0 mmol), and TMEDA (1.07 mL, 1.39 g, 12.0 mmol) was treated with $B(OMe)_3$ (2.73 mL, 2.50 g, 24.0 mmol). Normal workup afforded 2.03 g (92%) of product as a viscous oil that was used in the cross coupling reactions without further purification.

N,N-*Diethyl 2′,3′-dimethyldiphenyl-2-carboxamide (3a)*

According to general procedure B, 1-bromo-2,3-dimethylbenzene (1.36 mL, 1.85 g, 10.0 mmol) was subjected to reaction with 2-(*N*,*N*-diethylcarboxamido)phenylboronic acid (3.09 g, 14 mmol) in the presence of $Pd(PPh_3)_4$ (0.185 g, 0.16 mmol). Normal workup followed by flash chromatography (EtOAc–hexanes, 1:5) afforded 2.30 g (82%) of **3a** as colorless crystals, mp 68 to 69 °C (EtOAc). IR (KBr) (cm^{-1}): 1632. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.59 (br s, 3H), 0.80 (br s, 3H), 2.01 (s, 3H), 2.19 (s, 3H), 2.40–3.30 (br m, 3H), 3.65 (br s, 1H), 6.90–7.15 (m, 4H), 7.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 12.1, 14.0, 17.5, 20.9, 38.2, 42.8, 117.3, 118.9, 124.9, 127.5, 127.9, 128.6, 129.5, 130.1, 131.2, 135.0, 137.1, 137.6, 170.3. EI-MS *m*/*z* (rel. int.): 281 (M^+, 100), 209 (20), 181 (13), 165 (47), 74 (30). HR-MS *m*/*z* calcd. for $C_{19}H_{23}NO$: 281.1780; found: 281.1776.

1-Methyl-9-phenanthrol (4a)

According to general procedure C, treatment of a solution of *N*,*N*-diethyl 2′,3′-dimethylbiphenyl-2-carboxamide (2.81 g, 10 mmol) in THF (20 mL) with a solution of LDA (25.0 mmol) in THF (80 mL) followed by acidification, normal workup, and flash chromatography (hexane) afforded 1.98 g (95%) of **4a** as colorless crystals, mp 194–197 °C (CH_2Cl_2) (lit. (21) mp 199.5–200.5 °C (benzene)). IR (KBr) (cm^{-1}): 3307. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.61 (s, 3H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 6.8 Hz, 1H), 7.61–7.72 (m, 2H), 8.31 (d, *J* = 7.4 Hz, 1H), 8.53 (d, *J* = 7.8 Hz, 1H), 8.77 (d, *J* = 7.6 Hz, 1H), 10.39 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 20.5, 102.3, 121.7, 123.3, 123.9, 126.1, 128.0, 128.7, 132.2, 132.6, 132.9, 151.9. EI-MS *m*/*z* (rel. int.): 208 (M^+, 100), 178 (17), 165 (38), 152 (5), 89 (5), 76 (5).

1-Methylphenanthryl-9 trifluoromethanesulfonate (7a)

According to general procedure D, to a solution of 1-methyl-9-phenanthrol (**4a**) (1.04 g, 5.00 mmol) and 2,6-lutidine (0.69 mL, 0.64 g, 6.00 mmol) in CH_2Cl_2 was added triflic anhydride (1.01 mL, 1.69 g, 6.00 mmol). Normal workup followed by flash chromatography (hexane) afforded 1.62 g (95%) of **7a** as colorless crystals, mp 60 to 61 °C

(EtOAc). IR (KBr) (cm^{-1}): 1416, 1206, 1139. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.72 (s, 3H), 7.49 (s, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.71–7.77 (m, 2H), 7.91 (s, 1H), 8.15–8.21 (m, 1H), 8.47 (d, *J* = 6.9 Hz, 1H), 8.63–8.68 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.0, 114.8, 119.5 (q, *J* = 323 Hz), 121.2, 121.9, 123.7, 125.4, 127.8, 128.0, 129.1, 129.8, 130.1, 132.6, 135.8, 144.7. EI-MS *m/z* (rel. int.): 340 (M^+, 55), 207 (49), 179 (100), 152 (5), 69 (8). HR-MS *m*/z calcd. for $C_{16}H_{11}F_3O_3S$: 340.0381; found: 340.0387.

1-Methylphenanthrene (5a)

A stirred mixture of 1-methylphenanthryl-9 trifluoromethanesulfonate (**7a**) (0.340 g, 1.00 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh3, (10.5 mg, 0.04 mmol), Et_3N (0.303 g, 3.00 mmol), and HCO_2H (0.08 mL, 92 mg, 2.00 mmol) in DMF (10 mL) was heated at 60–70 °C for 30 min. The reaction mixture was cooled to rt, water was added, and the mixture was extracted with Et_2O. The combined organic layer was dried (Na_2SO_4), concentrated to dryness, and the residue was subjected to flash chromatography (hexane) to afford 96 mg (50%) of **6a** as colorless crystals, mp 118 to119 °C (hexane) (lit. (22) mp 120 to 121 °C (ethanol)). IR (KBr) (cm^{-1}): 1598. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.87 (s, 3H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.63–7.69 (m, 3H), 7.88 (d, *J* = 9.2 Hz, 1H), 8.01 (d, *J* = 9.2 Hz, 1H), 8.04 (t, *J* = 9.2 Hz, 1H), 8.69 (d, *J* = 8.1 Hz, 1H), 8.81 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.5, 121.4, 123.4, 123.5, 126.7, 127.1, 127.2, 128.3, 129.0, 130.9, 131.3, 132.2, 135.4. EI-MS *m/z* (rel. int.): 192 (M^+, 100), 165 (23), 150 (4), 139 (4), 95 (28), 83 (24).

Pinacolo[2-(*N,N*-diethylcarboxamido)-4-methylphenyl]boronate (2b)

According to general procedure A, a solution of *N*,*N*-diethyl-3-methylbenzamide (1.91 g, 10.0 mmol), *s*-BuLi (9.60 mL of a 1.25 mol L^{-1} solution,12.0 mmol), and TMEDA (1.07 mL, 1.39 g, 12.0 mmol) was treated with $B(OMe)_3$ (2.73 mL, 2.50 g, 24.0 mmol). Normal workup afforded a thick oil that was stirred with pinacol (2.83 g, 24.0 mmol) and $MgSO_4$ in dry CH_2Cl_2 for 12 h. Filtration and concentration of the filtrate gave a residue that was purified by flash chromatography (EtOAc–hexanes, 1:3) to afford 2.21 g (70%) of **2b** as a colorless oil. IR (neat) (cm^{-1}): 1633, 1432, 1350. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.88 (t, *J* = 7.2 Hz, 3H), 1.15 (s, 12H), 1.20 (t, *J* = 7.2 Hz, 3H), 2.20 (s, 3H), 3.02 (q, *J* = 7.2 Hz, 2H), 3.41 (q, *J* = 7.2 Hz, 2H), 6.90 (s, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.2, 14.4, 22.3, 25.5, 38.8, 43.6, 84.2, 123.1, 126.8, 129.2, 136.2, 141.7, 144.1, 172.5. EI-MS *m/z* (rel. int.): 316 (M^+ – H, 25), 302 (13), 259 (100), 218 (18), 174 (18), 144 (18), 177 (18), 83 (7), 55 (4). HR-MS *m/z* calcd. for $C_{18}H_{27}BNO_3$ (M^+ – H): 316.2084; found: 316.2093.

N,N-*Diethyl 3,2′,3′-trimethyldiphenyl-2-carboxamide (3b)*

According to general procedure B, 1-bromo-2,3-dimethylbenzene (1.36 mL, 1.85 g, 10.0 mmol) was subjected to reaction with **2b** (3.16 g, 10 mmol) in the presence of $Pd(PPh_3)_4$ (0.185 g, 0.16 mmol). Normal workup followed by flash chromatography (EtOAc–hexane, 1:5) afforded 1.89 g (64%) of **3b** as colorless crystals, mp 66–68 °C (EtOAc). IR (KBr) (cm^{-1}): 1630. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.65 (br, 3H), 0.75–1.00 (br, 3H), 2.28 (s, 3H), 2.48 (s, 3H), 2.50–3.30 (br, 4H), 3.65–3.85 (s, 1H), 6.98–7.23 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 12.0, 13.9, 17.4, 20.8, 21.3, 38.0, 42.7, 124.7, 127.4, 129.2, 130.0, 130.9, 131.6, 136.9, 137.1, 170.4. EI-MS *m/z* (rel. int.): 295 (M^+, 35), 222 (100), 177 (48), 180 (57), 165 (65), 74 (47). HR-MS *m/z* calcd. for $C_{20}H_{25}NO$: 295.1936; found: 295.1932.

1,7-Dimethyl-9-phenanthrol (4b)

According to general procedure C, treatment of a solution of **3b** (2.95 g, 10 mmol) in THF (20 mL) with a solution of LDA (25.0 mmol) in THF (80 mL) for 30 min followed by acidification, normal workup, and flash chromatography (hexane) afforded 1.78 g (80%) of **4b** as colorless crystals, mp 203–205 °C (CH_2Cl_2). IR (KBr) (cm^{-1}): 3351. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.54 (s, 3H), 2.59 (s, 3H), 7.20 (s, 1H), 7.30–7.39 (m, 2H), 7.51 (d, *J* = 9.0 Hz, 1H), 8.07 (s, 1H), 8.49 (d, *J* = 9.0 Hz, 1H), 8.65 (d, *J* = 9.0 Hz, 1H), 10.30 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 20.9, 22.4, 102.5, 121.8, 123.1, 124.0, 124.2, 126.4, 126.8, 128.6, 129.9, 130.4, 132.4, 133.0, 136.6, 151.9. EI-MS *m/z* (rel. int.): 222 (M^+, 100), 207 (7), 194 (13), 179 (41), 110 (3), 89 (3). HR-MS *m/z* calcd. for $C_{16}H_{14}O$: 222.1045; found: 222.1040.

1,7-Dimethylphenanthryl-9-trifluoromethanesulfonate (7b)

According to general procedure D, a solution of **4b** (1.11 g, 5.00 mmol) and 2,6-lutidine (0.69 mL, 0.64 g, 6.00 mmol) in CH_2Cl_2 was treated with triflic anhydride (1.01 mL, 1.69 g, 6.00 mmol). Normal workup followed by flash chromatography (hexane) afforded 1.42 (90%) g of **7b** as colorless crystals, mp 74 to 75 °C (EtOAc). IR (KBr) (cm^{-1}): 1421, 1215, 1140. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.64 (s, 3H), 2.75 (s, 3H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.57–7.64 (m, 2H), 7.72 (s, 1H), 7.74 (s, 1H), 8.53 (d, *J* = 8.4 Hz, 1H), 8.63 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.4, 22.5, 115.0, 119.5 (q, *J* = 315 Hz), 121.4, 121.7, 123.9, 125.8, 128.0, 128.9, 129.8, 130.6, 130.8, 136.0, 138.4, 144.9. EI-MS *m/z* (rel. int.): 354 (M^+, 38), 221 (39), 193 (100), 178 (20), 69 (7). H-MS *m/z* calcd. for $C_{17}H_{13}O_3F_3S$: 354.0538; found: 354.0545.

1,7-Dimethylphenanthrene (5b)

A stirred mixture of **7b** (0.354 g, 1.00 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), Et_3N (0.303 g, 3.00 mmol), and HCO_2H (0.08 mL, 92 mg, 2.00 mmol) in DMF (10 mL) was heated at 60–70 °C for 30 min, cooled to rt, and treated with water (10 mL). The resulting aqueous solution was extracted with Et_2O (3 × 10 mL), the combined organic extract was dried (Na_2SO_4) and concentrated in vacuo, and the residue was subjected to flash chromatography (hexane) to afford 175 mg (85%) of **5b** as colorless crystals, mp 83 to 84 °C (hexane) (lit. (23) mp 86 °C (ethanol)). ^1H NMR (300 MHz, $CDCl_3$) δ: 2.59 (s, 3H), 2.78 (s, 3H), 7.43–7.58 (m, 3H), 7.71 (s, 1H), 7.75 (d, *J* = 9.1 Hz, 2H), 7.90 (d, *J* = 9.1 Hz, 1H), 8.70 (d, *J* = 8.4 Hz, 1H), 8.62 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.4, 21.9, 121.2, 123.4, 126.5, 126.9, 127.8, 128.8, 129.0, 130.9, 131.0, 132.3, 135.3, 136.6. EI-MS *m/z* (rel. int.): 206 (M^+, 100), 192 (18), 179 96), 166 (6), 152 (5), 102 (6), 88 (5). HR-MS *m/z* calcd. for $C_{16}H_{14}$: 206.1096; found: 206.1090.

N,N-*Diethyl 4,2′,4′-trimethyldiphenyl-2-carboxamide (3c)*

According to general procedure B, 1-bromo-2,4-dimethylbenzene (0.27 mL, 0.37 g, 2.0 mmol) was subjected to reaction with pinacolo[2-(*N*,*N*-diethylcarboxamido)-4-methylphenyl]boronate (**2b**) (0.63 g, 2.0 mmol) in the presence of $Pd(PPh_3)_4$ (37 mg, 0.032 mmol). Normal workup followed by flash chromatography (EtOAc–hexane, 1:5) afforded 0.38 g (80%) of **3c** as a colorless oil. IR (neat) (cm^{-1}) 1633. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.60–0.90 (m, 6H), 2.20 (s, 3H), 2.32 (s, 3H), 2.40 (s, 3H), 2.50–3.90 (br, 4H), 6.90–7.30 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.6, 21.5, 21.5, 126.2, 128.1, 128.6, 129.3, 130.1, 130.7, 131.2, 135.0, 135.1, 137.3, 137.4, 137.6, 170.8. EI-MS *m*/*z* (rel. int.): 294 (18), 265 (64), 74 (70). HR-MS *m*/*z* calcd. for $C_{20}H_{25}NO$: 295.1936; found: 295.1930.

2,7-Dimethyl-9-phenanthrol (4c)

According to general procedure C, treatment of a solution of (**3c**) (0.30 g, 1.0 mmol) in THF (10 mL) with a solution of LDA (2.5 mmol) in THF (10 mL) for 30 min followed by acidification, normal workup, and flash chromatography (hexane) afforded 0.21 g (94%) of **4c** as colorless crystals, mp 154 to 155 °C (CH_2Cl_2). IR (KBr) (cm^{-1}): 3545. ^1H NMR (500 MHz, $CDCl_3$) δ: 2.46 (s, 3H), 2.53 (s, 3H), 7.00 (s, 1H), 7.25 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.49 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.50 (s, 1H), 8.05 (s, 1H), 8.48 (d, *J* = 8.5 Hz, 1H), 8.58 (d, *J* = 8.5 Hz, 1H), 10.21 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 22.0, 22.1, 105.5, 122.9, 123.2, 124.2, 126.0, 126.7, 126.8, 129.5, 129.8, 133.6, 135.9, 136.5, 151.5. EI-MS *m*/*z* (rel. int.): 223 (100), 208 (30). HR-MS *m*/*z* calcd. for $C_{16}H_{14}O$: 222.1045; found: 222.1039.

2,7-Dimethylphenanthryl-9 trifluoromethanesulfonate (7c)

According to general procedure D, a solution of **4c** (0.11 g, 0.50 mmol) and 2,6-lutidine (0.07 mL, 0.064 g, 0.60 mmol) in CH_2Cl_2 was treated with triflic anhydride (0.10 mL, 0.17 g, 0.60 mmol). Normal workup followed by flash chromatography (hexane) afforded 0.17 g (95%) of **7c** as colorless crystals, mp 138 to 139 °C (hexane). IR (KBr) (cm^{-1}): 1430. ^1H NMR (500 MHz, $CDCl_3$) δ: 2.58 (s, 3H), 2.63 (s, 3H), 7.53 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.58 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.66 (s, 1H), 7.68 (s, 1H), 7.92 (s, 1H), 8.51 (*J* = 8.0 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.8, 22.2, 118.0, 119.2 (q, *J* = 318 Hz), 121.5, 122.9, 123.2, 125.5, 127.9, 128.9, 130.0, 130.3, 130.6, 137.6, 137.8, 144.71. EI-MS *m*/*z* (rel. int.): 354 (5), 221 (22), 193 (100), 178 (25), 69 (24). HR-MS *m*/*z* calcd. for $C_{17}H_{13}O_3F_3S$: 354.0538; found: 354.0540.

2,7-Dimethylphenanthrene (5c)

A stirred mixture of **7c** (0.035 g, 0.10 mmol), $Pd(OAc)_2$ (0.5 mg, 0.02 mmol), PPh_3 (1.0 mg, 0.004 mmol), Et_3N (0.030 g, 0.30 mmol), and HCO_2H (0.01 mL, 9 mg, 0.20 mmol) in DMF (2 mL) was heated at 60–70 °C for 30 min, cooled to rt, and treated with water (2 mL). The resulting aqueous solution was extracted with Et_2O (3 × 2 mL), the combined organic layer was dried (Na_2SO_4) and concentrated in vacuo, and the residue was subjected to flash chromatography (hexane) to afford 18 mg (91%) of **5c** as colorless crystals, mp 100 to 101 °C (hexane) (lit. (24*a*) mp 101 to 102 °C (ethanol); lit. (24*b*) mp 101 to 102 °C (methanol)). ^1H NMR (25) (500 MHz, $CDCl_3$) δ: 2.60 (s, 6H), 7.50 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.69 (s, 2H), 7.70 (s, 2H), 8.58 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.9, 122.8, 127.1, 128.5, 128.6, 128.7, 132.3, 136.2. EI-MS *m*/*z* (rel. int.): 206 (100), 191 (46), 189 (47), 178 (19), 69 (20).

3-Ethylphenyltrifluoromethanesulfonate (9)

According to method D, a solution of 3-ethylphenol (**8**) (1.22 g, 10.00 mmol) and 2,6-lutidine (1.40 mL, 1.28 g, 12.00 mmol) in CH_2Cl_2 (100 mL) was treated with triflic anhydride (2.01 mL, 3.38 g, 12.00 mmol). Normal workup followed by flash chromatography (hexane) afforded 2.28 g (90%) of **9** as a colorless oil. IR (neat) (cm^{-1}): 1424, 1214, 1143. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.29 (t, *J* = 8.4 Hz, 3H), 2.73 (q, *J* = 8.4 Hz, 2H), 7.14 (s, 1H), 7.19–7.34 (m, 2H), 7.38 (t, *J* = 15.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 15.4, 28.9, 118.8, 119.2 (q, *J* = 315 Hz), 121.0, 129.4, 130.4, 147.6, 150.1. EI-MS *m*/*z* (rel. int.): 254 (M^+, 100), 174 (75), 121 (47), 91 (90), 77 (22), 65 (8), which showed identical ^1H NMR, ^{13}C NMR, and MS spectra to those reported for authentic material (26).

N,N-*Diethyl 3-ethylbenzamide (10)*

A stirred mixture of **9** (0.254 g, 1.00 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), dppf (33 mg, 0.06 mmol), Et_3N (0.42 mL, 0.303 g, 2.00 mmol), and Et_2NH (2.06 mL, 1.46 g, 20.0 mmol) in DMF (10 mL) was heated at 60–70 °C for 12 h, cooled to rt, and treated with water (10 mL). The aqueous portion was extracted with Et_2O (3 × 10 mL) and the extract was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash column chromatography (EtOAc–hexane, 1:5) to afford 0.140 g (70%) of **10** as a yellow oil. IR (neat) (cm^{-1}): 1633. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.00–1.20 (br, 6H), 1.17 (t, *J* = 7.2 Hz, 3H), 2.60 (q, *J* = 7.2 Hz, 2H), 3.17 (br s, 2H), 3.48 (br s, 2H), 7.08–7.27 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.2, 14.6, 15.7, 29.1, 39.5, 43.6, 123.7, 126.7, 128.9, 137.6, 144.7, 171.8. EI-MS *m*/*z* (rel. int.): 205 (M^+, 58), 176 (7), 133 (100), 105 (28), 77 (17). HR-MS *m*/*z* calcd. for $C_{13}H_{19}NO$: 205.1467; found: 205.1469.

Pinacolo[2-(*N,N*-diethylcarboxamido)-3-ethylphenyl]boronate (11)

According to general procedure A, a solution of **10** (2.05 g, 10.0 mmol), *s*-BuLi (9.60 mL of a 1.25 mol L^{-1} solution, 12.0 mmol), and TMEDA (1.07 mL, 1.39 g, 12.0 mmol) was treated with $B(OMe)_3$ (2.73 mL, 2.50 g, 24.0 mmol). Normal workup afforded a thick oil that was stirred with a solution of pinacol (2.83 g, 24.0 mmol) and anhyd $MgSO_4$ (5 g) in dry CH_2Cl_2 (20 mL). Filtration followed by concentration gave a residue that was purified by flash chromatography (EtOAc–hexane, 1:3) to afford 2.51 g (76%) of **11** as a colorless oil. IR (neat) (cm^{-1}): 1635, 1432, 1354. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.01 (t, *J* = 7.5 Hz, 3H), 1.20 (t, *J* = 8.1 Hz, 3H), 1.25–1.30 (m, 15H), 2.63 (q, *J* = 7.5 Hz, 2H), 3.14 (q, *J* = 8.1 Hz, 2H), 3.55 (q, *J* = 8.1 Hz, 2H), 7.06 (s, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 12.9, 14.1, 15.6, 25.2, 38.5, 43.3, 83.9, 125.4, 127.7, 135.9, 143.9, 149.9, 171.0. EI-MS *m*/*z* (rel. int.): 331 (M^+, 21), 273 (100), 232 (16), 188 (6), 158 (7), 105 (8), 55 (4). HR-MS *m*/*z* calcd. for $C_{19}H_{30}BNO_3$: 331.2319; found: 331.2321.

N,N-*Diethyl 3-ethyl-2′,3′-dimethylbiphenyl-2-carboxamide (12)*

According to general procedure B, 1-bromo-2,3-dimethylbenzene (1.36 mL, 1.85 g, 10.0 mmol) was subjected to reaction with **11** (3.31 g, 10 mmol) in the presence of $Pd(PPh_3)_4$ (0.185 g, 0.16 mmol). Normal workup followed by flash chromatography (EtOAc–hexane, 1:5) afforded 1.85 g (60%) of **12** as a viscous oil. IR (neat) (cm^{-1}): 1634. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.68 (s, 3H), 0.75–1.04 (br, 3H), 1.28 (t, *J* = 7.8 Hz, 3H), 2.08 (s, 3H), 2.27 (s, 3H), 2.72 (q, *J* = 7.8 Hz, 2H), 2.75–3.30 (br, 4H), 3.73 (s, 1H), 6.96–7.25 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 12.1, 14.1, 15.6, 17.6, 20.9, 28.8, 38.2, 42.8, 125.4, 126.8, 128.0, 129.4, 130.1, 135.1, 137.2, 143.5, 170.8. EI-MS *m/z* (rel. int.): 309 (M^+, 100), 280 (13), 237 (15), 209 (8), 178 (18), 165 (15), 74 (35). HR-MS *m/z* calcd. for $C_{21}H_{27}NO$: 309.2093; found: 309.2086.

7-Ethyl-1-methyl-9-phenanthrol (13)

According to general procedure C, treatment of a solution of **12** (3.09 g, 10 mmol) in THL (20 mL) with a solution of LDA (25.0 mmol) in THF (80 mL) for 30 min followed by acidification, normal workup, and flash chromatography (hexane) afforded 2.24 g (95%) of **13** as colorless crystals, mp 192–195 °C (CH_2Cl_2). IR (KBr) (cm^{-1}): 3306. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.28 (t, *J* = 8.1 Hz, 3H), 2.60 (s, 3H), 2.84 (q, *J* = 8.1 Hz, 2H), 7.25 (s, 1H), 7.28–7.38 (m, 2H), 7.51 (d, *J* = 8.4 Hz, 1H), 8.12 (s, 1H), 8.47 (d, *J* = 8.1 Hz, 1H), 8.63 (d, *J* = 8.1 Hz, 1H), 10.36 (s, 1H). ^{13}C NMR (75M Hz, $CDCl_3$) δ: 16.4, 20.5, 29.2, 102.1, 121.5, 123.7, 124.0, 126.1, 126.6, 127.4, 128.2, 128.4, 130.4, 132.2, 132.7, 142.5, 151.8. EI-MS *m/z* (rel. int.): 236 (M^+, 100), 221 (65), 207 (10), 193 (15), 179 (10), 165 (4), 89 (3). HR-MS *m/z* calcd. for $C_{17}H_{16}O$: 236.1201; found: 236.1206.

7-Ethyl-1-methylphenanthryl-9-trifluoromethanesulfonate (14)

According to general procedure D, a solution of **13** (1.18 g, 5.00 mmol) and 2,6-lutidine (0.69 mL, 0.64 g, 6.00 mmol) in CH_2Cl_2 (100 mL) was treated with triflic anhydride (1.01 mL, 1.69 g, 6.00 mmol). Normal workup followed by flash chromatography (hexane) afforded 1.20 g (95%) of **14** as colorless crystals, mp 61 to 62 °C (EtOAc). IR (KBr) (cm^{-1}): 1421, 1208, 1135. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.41 (t, *J* = 7.5 Hz, 3H), 2.74 (s, 3H), 2.95 (q, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.57–7.66 (m, 2H), 7.91 (s, 1H), 7.97 (s, 1H), 8.52 (d, *J* = 9.0 Hz, 1H), 8.64 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 15.7, 20.1, 29.4, 114.7, 119.3 (q, *J* = 323 Hz), 120.1, 121.1, 123.7, 129.3, 129.5, 130.2, 130.7, 135.7, 144.3, 144.7. EI-MS *m/z* (rel. int.): 368 (M^+, 35), 235 (45), 207 (100), 192 (18), 165 (3), 69 (7). HR-MS *m/z* calcd. for $C_{18}H_{15}F_3O_3S$: 368.0684; found: 368.0689.

7-Ethyl-1-methylphenanthrene (15)

A stirred mixture of **14** (0.368 g, 1.00 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), Et_3N (0.42 mL, 0.303 g, 3.00 mmol), and HCO_2H (0.08 mL, 92 mg, 2.00 mmol) in DMF (10 mL) was heated at 60–70 °C for 30 min. The reaction mixture was cooled to rt and water was added (10 mL). The aqueous layer was separated and extracted with Et_2O (3 × 10 mL), and the extract was dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash column chromatography (hexane) to afford 202 mg (92%) of **15** as colorless crystals, mp 92 to 93 °C (hexane) (lit. (27) mp 87.5 °C (MeOH)). ^1H NMR (300 MHz, $CDCl_3$) δ: 1.47 (t, *J* = 7.5 Hz, 3H), 2.84 (s, 3H), 2.96 (q, *J* = 7.5 Hz, 2H), 7.48–7.65 (m, 3H), 7.78 (s, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 8.63 (d, *J* = 9.0 Hz, 1H), 8.69 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 16.1, 20.4, 29.2, 121.2, 123.2, 123.4, 126.5, 127.0, 127.2, 127.7, 127.8, 129.2, 130.8, 130.9, 132.3, 135.2, 142.9. EI-MS *m/z* (rel. int.): 220 (M^+, 100), 205 (73), 189 (15), 178 (3), 165 (3), 101 (4). HR-MS *m/z* calcd. for $C_{17}H_{16}$: 220.1252; found: 220.1255.

N,N-*Diethyl 4-*tert*-butylphenyl carbamate (23)*

To a suspension of sodium hydride (0.48 g, 60% in mineral oil, 12 mmol) in anhyd THF (20 mL) was added 4-*tert*-butylphenol (1.50 g, 10 mmol). After hydrogen evolution ceased (1 h), diethylcarbamoyl chloride (1.51 mL, 1.62 g, 12 mmol) was added and the reaction mixture was stirred at rt for 2 h, and treated with water (10 mL). The aqueous layer was separated and extracted with Et_2O (3 × 20 mL). The combined extract was dried (Na_2SO_4) and concentrated in vacuo to give a residue that was purified by flash column chromatography (EtOAc–hexane, 1:3) to afford 1.49 g (60%) of **23** as colorless crystals, mp 77 to 78 °C (CH_2Cl_2) (lit. (28) mp 86 °C (pentene)). IR (KBr) (cm^{-1}): 1706, 1480, 1402, 1277, 1211. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.25 (s, 6H), 1.34 (s, 9H), 3.43 (s, 4H), 7.04–7.10 (m, 2H), 7.36–7.42 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.8, 14.6, 31.8, 34.7, 42.2, 42.6, 121.4, 126.4, 148.1, 149.6, 154.8. EI-MS *m/z* (rel. int.): 249 (M^+, 35), 163 (2), 146 (2), 135 (3), 100 (100), 72 (7). HR-MS *m/z* calcd. for $C_{15}H_{23}NO_2$: 249.1729; found: 249.1736.

N,N-*Diethyl 4-tert-butyl-2-hydroxybenzamide (24)*

A solution of **23** (2.49 g, 10.0 mmol) in anhyd THF (20 mL) was added dropwise to a solution of *s*-BuLi (9.6 mL of 1.25 mol L^{-1} solution, 12.0 mmol) and TMEDA (1.07 mL, 1.39 g, 12.0 mmol) in anhyd THF (30 mL) at –78 °C. The reaction mixture was stirred at –78 °C for 1 h, allowed to warm to rt over 12 h, and quenched with a satd. aq. NH_4Cl solution (10 mL). The aqueous layer was separated and extracted with Et_2O (3 × 20 mL), and the combined extract was dried (Na_2SO_4) and concentrated in vacuo. The resulting residue was purified by flash column chromatography (EtOAc–hexanes, 1:5) to afford 1.37 g (55%) of **24** as colorless crystals, mp 133 – 135 °C (CH_2Cl_2). IR (KBr) (cm^{-1}): 3142, 1595, 1268. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.27–1.33 (m, 15H), 3.51 (q, *J* = 7.2 Hz, 4H), 6.92 (d, *J* = 17.1 Hz, 1H), 7.27 (d, *J* = 5.0 Hz, 1H) 7.34 (dd, *J* = 17.1, 5.0 Hz, 1H), 9.50 (s, 1H). $^{13}CNMR$ (75 MHz, $CDCl_3$) δ:13.8, 31.8, 34.4, 42.5, 117.6, 118.1, 124.3, 129.6, 141.4, 156.4, 172.2. EI-MS *m/z* (rel. int.): 249 (M^+, 31), 234 (72), 177 (76), 161 (100), 133 (16), 105 (20), 72 (38). HR-MS *m/z* calcd. for $C_{15}H_{23}NO_2$: 249.1729; found: 249.1719.

4*-tert-*Butyl-2-(*N,N-*diethylcarboxamido)phenyl trifluoromethanesulfonate (20)

According to general procedure D, a solution of **24** (2.49 g, 10.0 mmol) and pyridine (0.97 mL, 0.95 g, 12.0 mmol) in CH_2Cl_2 (100 mL) was treated with triflic an-

hydride (2.01 mL, 3.38 g, 12.0 mmol). Normal workup followed by flash chromatography (EtOAc–hexane, 1:5) afforded 2.48 g (65%) of **20** as a colorless oil. IR (neat) (cm^{-1}): 1645, 1426, 1215. ^1H NMR ($CDCl_3$) δ: 1.08 (t, J = 7.2 Hz, 3H), 1.17 (t, J = 7.2 Hz, 3H), 1.30 (s, 9H), 3.16 (q, J = 7.2 Hz, 2H), 3.40–3.70 (br, 2H), 7.23 (d, J = 8.6 Hz, 1H), 7.37 (d, J = 2.1 Hz, 1H), 7.40 (dd, J = 8.6, 2.1 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 12.7, 14.2, 31.4, 35.1, 39.5, 43.3, 118.8 (q, J = 323 Hz), 121.5, 125.8, 128.0, 130.7, 143.3, 152.1, 166.2. EI-MS m/z (rel. int.): 382 (M^+, 71), 309 (100), 233 (38), 161 (73), 72 (69). HR-MS m/z calcd. for $C_{16}H_{22}F_3NO_4S$: 381.1222; found: 381.1234.

N,N-*Diethyl 3*-tert-*butyl-2′,3′-trimethyldiphenyl-2-carboxamide (19)*

According to general procedure B, 2,3-dimethylphenylboronic acid (1.50 g, 10.0 mmol) was subjected to reaction with **20** (3.82 g, 10 mmol) in the presence of $Pd(PPh_3)_4$ (0.185 g, 0.16 mmol). Normal workup followed by flash chromatography (EtOAc–hexane, 1:5) afforded 2.76 g (82%) of **19** as a viscous oil. IR (cm^{-1}): 1634. ^1H NMR ($CDCl_3$) δ: 0.69 (t, J = 7.2 Hz, 3H), 0.70–1.0 (br, 3H), 1.35 (s, 9H), 2.10 (s, 3H), 2.27 (s, 3H), 2.50–3.90 (br m, 4H), 6.80–7.43 (m, 6H). ^{13}C NMR ($CDCl_3$) δ: 12.2, 13.8, 24.1, 31.6, 34.9, 38.3, 124.4, 125.4, 126.5, 127.6, 128.4, 129.3, 134.7, 137.1, 142.6, 150.3, 151.6, 155.5, 171.1. EI-MS m/z (rel. int.): 337 (M^+, 97), 322 (7), 264 (100), 250 (37), 209 (40), 181 (12), 165 (17), 74 (32). HR-MS m/z calcd. for $C_{23}H_{31}NO$: 337.2406; found: 337.2398.

7*-tert-*Butyl-1-methyl-9-phenanthrol (25)

According to general procedure C, treatment of a solution of **19** (3.37 g, 10 mmol) in THF (20 mL) with a solution of LDA (25.0 mmol) in THF (80 mL) for 30 min followed by acidification, normal workup, and flash chromatography (hexane) afforded 2.38 g (90%) of **25** as a powder that gave colorless crystals, mp 165–168 °C (CH_2Cl_2). IR (KBr) (cm^{-1}): 3466. ^1H NMR ($CDCl_3$) δ: 1.53 (s, 9H), 2.63 (s, 3H), 5.81 (s, 1H), 7.20 (s, 1H), 7.38–7.45 (m, 2H), 7.81 (dd, J = 8.1, 2.1 Hz, 1H), 8.36 (d, J = 2.1 Hz, 1H), 8.49 (d, J = 8.1 Hz, 1H), 8.64 (d, J = 9.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 20.6, 31.1, 35.7, 103.4, 118.4, 121.3, 123.6, 124.3, 125.5, 126.2, 127.3, 128.2, 130.5, 131.9, 133.4, 149.9, 150.3. EI-MS m/z (rel. int.): 264 (M^+, 100), 250 (50), 232 (13), 221 (22), 194 (13), 179 (12), 165 (9), 11 (8). HR-MS m/z calcd. for $C_{19}H_{20}O$: 264.1514 (accurate data could not be obtained due to oxidation of the sample).

7*-tert-*Butyl-1-methylphenanthryl-9-trifluoromethanesulfonate (26)

According to general procedure D, to a solution of **25** (1.32 g, 5.00 mmol) and 2,6-lutidine (0.69 mL, 0.64 g, 6.00 mmol) in CH_2Cl_2 (100 mL) was added triflic anhydride (1.01 mL, 1.69 g, 6.00 mmol). Normal workup followed by flash chromatography (hexane) afforded 1.72 g (87%) of **26** as colorless crystals, mp 103 to 104 °C (EtOAc). IR (KBr) (cm^{-1}): 1423, 1207, 1139. ^1H NMR ($CDCl_3$) δ: 1.61 (s, 9H), 2.73 (s, 3H), 7.45 (d, J = 7.2 Hz, 1H), 7.56 (t, J = 8.4 Hz, 1H), 7.88 (dd, J = 9.0, 1.8 Hz, 1H), 7.93 (s, 1H), 8.27 (d, J = 1.8 Hz, 1H), 8.44 (d, J = 8.1 Hz, 1H), 8.66 (d, J = 9.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 20.0, 31.6, 35.5, 114.7, 117.6, 119.4 (q, J = 323 Hz), 121.1, 123.6, 125.1, 126.9, 127.7, 128.7, 129.6, 130.1, 130.6, 135.6, 144.9, 151.2. EI-MS m/z (rel. int.): 396 (M^+, 68), 381 (14), 263 (100), 236 (75), 220 (32), 205 (16), 179 (8), 69 (11). HR-MS m/z calcd. for $C_{20}H_{19}F_3O_3S$: 396.1007; found: 396.1008.

7*-tert-*Butyl-1-methylphenanthrene (27)

A stirred mixture of **26** (0.396 g, 1.00 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), Et_3N (0.42 mL, 0.303 g, 3.00 mmol), and HCO_2H (0.08 mL, 92 mg, 2.00 mmol) in DMF (10 mL) was heated at 60–70 °C for 30 min. The reaction mixture was cooled to rt, water (0 mL) was added, and the mixture was extracted with Et_2O (3 × 10 mL). The combined organic extract was dried (Na_2SO_4), concentrated to dryness, and the residue was subjected to flash chromatography (hexane) to afford 248 mg (95%) of **27** as colorless crystals, mp 126 to 127 °C (hexane). ^1H NMR ($CDCl_3$) δ: 1.74 (s, 9H), 2.96 (s, 3H), 7.64 (d, J = 7.4 Hz, 1H), 7.74 (t, J = 7.5 Hz, 1H), 7.93 (dd, J = 8.6, 1.8 Hz, 1H), 7.98 (d, J = 9.3 Hz, 1H), 8.12 (s, 1H), 8.14 (d, J = 9.2 Hz, 1H), 8.77 (d, J = 8.6 Hz, 1H), 8.82 (d, J = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 20.5, 32.0, 35.3, 121.7, 123.7, 125.8, 126.9, 127.9, 128.2, 129.4, 131.2, 131.5, 132.6, 135.6, 150.0. EI-MS m/z (rel. int.): 248 (M^+, 100), 234 (95), 218 (10), 205 (13), 189 (7), 178 (3). HR-MS m/z calcd. for $C_{19}H_{20}$: 248.1565; found: 248.1564.

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