Regiospecific Synthesis of Dimethylphenanthrenes

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ABSTRACT
The dimethylated phenanthrenes 2,3-dimethylphenanthrene (4a), 2,7-dimethylphenanthrene (4b), 2,6-dimethylphenanthrene (4c) and 1,7-dimethylphenanthrene (4d) have been prepared in gram-quantities by a short sequence of directed ortho metalation (DoM) of N,N-diethylbenzamides followed by Suzuki–Miyaura cross-coupling reaction and directed remote metalation (DreM) to form 9-phenanthrols. The final phenanthrenes were obtained through protection/deprotection as triflates.

Introduction
Polycyclic aromatic hydrocarbons (PAHs) are the primary cause of chronic toxicity of petroleum products to marine fish, and crude oil and discharges from the oil and gas industry contain large quantities and a very large array of PAHs (1). Even with the decades of research, only a very small portion of these PAHs, and mainly the basic ring-systems, have been described (2). A majority and sometimes up to 80–90% of all petrogenic PAHs are alkylated (3, 4). Alkylated PAHs are more persistent in weathering processes and microbial degradation with increasing number of substituents (5–7). The toxicity of PAHs does not arise from the parent compounds, but from the metabolites (8, 9). To complicate things further, different organisms produce different arrays of metabolites with different toxicities from the same parent compound (10, 11). A methyl group can block oxidation even in the remote positions and change the metabolic profile (12, 13). These effects are still poorly elucidated, but alkylated phenanthrenes are known to be more toxic than phenanthrene (14), and the position of the alkyl groups on PAHs affects the toxicity toward fish embryos (15). Another example is 5-methylchrysene where the substitution makes the compound 1000 times more carcinogenic than chrysene, although substitution in other positions gives less dramatic effects (16).

Recently, it was found that the benthic invertebrate N. diversicolor mainly metabolized methylated phenanthrenes and chrysenes to the corresponding acids (17). Again, the position of the methyl group had an effect. To further study the effect of the position of methyl groups in exposure studies, Malmquist and Christensen (18) proposed a set of 5 dimethylated phenanthrenes: 2,3-dimethylphenanthrene (4a), 2,7-dimethylphenanthrene (4b), 2,6-dimethylphenanthrene (4c), 1,7-dimethylphenanthrene (4d) and 1,9-methylphenanthrene. Although these compounds are commercially available as analytical standards, there are no feasible sources for the multi-mg quantities desired in exposure studies. Thus, we decided to make/ remake these compounds and report the synthesis herein.

Although the classical Pschorr synthesis of phenanthrenes (19) was developed as early as 1896 (20), it has dominated the synthesis of simple phenanthrenes for a long time, but the need for better control of substitutions on the phenanthrene ring has led to the development of several different synthetic approaches. Ring-closure of stilbenes by photochemical oxidation in the Mallory-reaction (21)
is often effective, but affords a mixture of isomers for meta-substituted stilbenes. A similar reaction can be achieved with mCPBA (22), but with more restrictions on the substitutions. Another main route to the simple substituted phenanthrenes is the combination of directed ortho metalation (DoM), Suzuki–Miyaura cross-coupling and directed remote metalation (DreM) to form phenanthrenes (23). This reaction sequence has been used successfully to make a wide range of substituted phenanthrenes (24, 25). Herein, we present a scale-up of the Snieckus route (24) to 4b and 4c and utilize its flexibility to make 4a and 4d.

Phenanthrenes are found in a range of different molecules from various sources and for a number of applications, and several other methods have been utilized in their synthesis. A more extensive discussion of their applications and synthesis can be found in Wang et al. (26) and Jørgensen et al. (25).

**Results and discussion**

Only 1,9-dimethylphenanthrene can easily be made as a single isomer by photochemical cyclization, and its synthesis will be reported elsewhere with other compounds following the photochemical cyclization of biphenyls. For compounds 4a–d, a selectivity problem due to meta-substitution will produce a mix of isomers by following the photochemical cyclization protocol. Thus, the most practical approach will be through DreM reaction from biphenyls as presented in Scheme 1.

**Scheme 1.** Synthesis of dimethylphenanthrenes 4a–d.

Borane 1a was readily available by DoM of diethylbenzamide followed by addition of triisopropyl borate. Contrarily to quenching by trimethyl borate (24), triisopropyl boronates does not hydrolyze to boronic acid during work-up, but is readily cross-coupled in the following step. In the previously described reaction (24) of N,N-diethyl-3-methylbenzamide with trimethyl borate, purification by flash column chromatography of the pinacol ester was necessary. With triisopropyl borate, there was no trace of substitution in the 2-position and the crude product could be used in the cross-coupling without any further purification. Standard Suzuki–Miyaura cross-coupling of the boronate in slight excess (1.25 equivalents) with the required bromobenzene catalyzed by 5 mol% PdCl₂(dppf) in aqueous solvent provided biphenyl 2a in 73% yield. The other cross-couplings were performed with 2 equivalents boronate, but this excess should not be necessary. For biphenyl 2c, only 42% yield was obtained in the cross-coupling reaction. However, biphenyl 2c was the last compound made in this project, and as the other bromobenzenes used in the cross-coupling reactions are both more and less bulky, it is reasonable to
assume that a repeat experiment would have produced better results. Our spectral data of biphenyl 2d deviate from those reported by Cai (24). From a DreM reaction of biphenyl 2a–d using freshly made LDA (23), (diisopropylamide and n-BuLi) 9-phenanthrols were formed. 9-Phenanthrols are easily oxidized to the corresponding brown colored quinones when purified by flash chromatography. In order to avoid this problem, the alcohol was protected directly after extraction before further purification. The right protecting group can serve a double purpose as it can easily be cleaved from the phenanthrene to remove the oxygen left after the DreM reaction. Although the less expensive way of doing this is through a carbamate (25), the more commonly used triflate was used since the cleavage of carbamate inevitably produce a few percent of the alkylated byproduct that would be inseparable from the product by moderate resolution chromatography. The DreM reaction followed by protection with triflic anhydride using 2,6-lutidine as base gave triflates 3a–d in 67–75% yield. While the data of triflate 3b are in accordance with those reported by Cai (24), there is a small difference in the $^1H$ NMR data at 7.9 and 7.7 ppm for triflate 3d. When converted to 4d, all the data are in accordance. Cleavage of the triflates with palladium and formic acid as hydrogen source gave the target compounds 4a–d in close to quantitative yields after flash column chromatography.

In summary, this short route provided the desired dimethylphenanthrenes as single isomers in gram-scale after only three chromatographic purifications and in reasonable over all yields (29–62% calculated from the bromobenzene cross-coupling partners, or 14–31% as calculated from the benzamides).

**Experimental**

**General**

The reactions were followed by TLC on silica plates (60A, F$_{254}$). Flash column chromatography was performed with silica gel (40–63 μm, 60A). All melting points (Mp) were measured in capillary tubes on a Bibby SMP3 Mp apparatus. NMR-spectroscopy was performed on a Varian Mercury 300 MHz spectrometer. The FID’s were treated on MestReNova or MestReNova Lite for integration and peak picking. Infrared spectroscopy was performed on a PerkinElmer, Spectrum One FT-IR spectrometer. HRMS were obtained from the University of Bergen or the Arctic University of Norway by electron impact (EI) or electrospray ionization (ESI) on time-of-flight (TOF) mass analyzers.

All reactions were performed under the nitrogen atmosphere. In Suzuki–Miyaura reactions with PdCl$_2$(dppe), all solvents were degassed by freeze-thaw cycles.

$N,N$-diethylbenzamide was made as described by Hall’s group (27), and afforded 9.86 g (86%) as a clear oil by vacuum distillation at 116°C, 3.7 mBar. $N,N$-Diethyl-3-methylbenzamide and the differently methylated bromobenzenes were purchased from Sigma-Aldrich. (Abbreviations – DCM: dichloromethane, DME: dimethoxy ethane, DMF: dimethylformamide, EtOAc: ethyl acetate, Et$_2$O: diethyl ether, PE: petroleum ether, THF: tetrahydrofuran, TMEDA: tetramethylethylenediamine).

**Bis(propan-2-yl)[2-(diethylcarbamoyl)phenyl]boronate (1a)**

A solution of $N,N$-diethylbenzamide (5.48 g, 30.9 mmol) in anhydrous THF (100 mL) was added dropwise to a solution of s-BuLi (41.2 mL (0.9 M), 37.1 mmol), and TMEDA (5.56 mL, 37.1 mmol) in anhydrous THF (100 mL) at −78°C. After 1 h stirring at −78°C, the mixture was treated with triisopropyl borate (17.8 mL, 77.3 mmol). The mixture was allowed to reach room temperature overnight, quenched with sat. aq. NH$_4$Cl solution (150 mL) and extracted with Et$_2$O (3 × 150 mL). The combined organic phase was dried over MgSO$_4$, filtered and concentrated under reduced pressure to give 7.75 g (82%) of 1a as a brown oil. The compound was partly hydrolyzed and had a complex $^1H$ NMR spectrum including different rotamers and was not assigned in detail. The crude compound was used in the next step without further purification.

**Bis(propan-2-yl)[2-(diethylcarbamoyl)-4-methylphenyl]boronate (1b)**

A solution of $N,N$-diethyl-3-methylbenzamide (5.25 g, 27.5 mmol) in anhydrous THF (80 mL) was added dropwise to a solution of s-BuLi (62.2 mL (0.53 M), 32.9 mmol), and TMEDA (4.94 mL, 32.9 mmol)
in anhydrous THF (80 mL) at −78°C. After 1 h stirring at −78°C, the mixture was treated with 3-isopropylborate (15.7 g, 68.6 mmol). The mixture was allowed to reach room temperature overnight, quenched with sat. aq. NH₄Cl solution (150 mL) and extracted with Et₂O (3 × 150 mL). The combined organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure to give 8.82 g (quant.) of 1b as a brown oil. The compound was partly hydrolyzed and had a complex ¹H NMR spectrum including different rotamers and was not assigned in detail. The crude compound was used in the next step without further purification.

**N,N-diethyl-2-(2,4,5-trimethylphenyl)benzamide (2a)**

A mixture of PdCl₂(dppf) (0.86 g, 1.05 mmol) and 5-bromo-1,2,4-trimethylbenzene (4.17 g, 20.9 mmol) in DME (60 mL) was stirred at room temperature for 15 min before 1a (7.75 g, 25.4 mmol) in DME (40 mL) was added, followed by the addition of 2M aq. Na₂CO₃ (60 mL). The mixture was boiled at reflux for 18 h, cooled and extracted with Et₂O (3 × 150 mL). The combined organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure to afford 4.53 g (73%) of 2a as a brown oil. ¹H NMR (300 MHz, CDCl₃) δ: 0.65–1.00 (m, 6H), 2.09–2.25 (m, 9H), 2.84 (br s, 2H), 3.75 (br s, 2H), 7.00 (br s, 1H), 7.23 (br s, 1H), 7.34–7.41 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ: 11.6, 13.7, 19.1, 19.3, 19.6, 37.8, 42.4, 127.0, 128.1, 130.4, 131.4, 135.7, 137.1, 170.3; IR (KBr, cm⁻¹): 1634, 1456, 1427; HRMS (ESI-TOF) m/z [M+H]⁺ for C₂₀H₂₅NO calcd 296.20144, found 296.20166.

**2-(2,4-dimethylphenyl)-N,N-diethyl-5-methylbenzamide (2b)**

A mixture of PdCl₂(dppf) (0.58 g, 0.71 mmol) and 1-bromo-2,4-dimethylbenzene (2.62 g, 14.2 mmol) in DME (60 mL) was stirred at room temperature for 15 min before 1b (8.82 g, 27.6 mmol) in DME (40 mL) was added, followed by the addition of 2M aq. Na₂CO₃ (60 mL). Reaction and workup as described for 2a afforded 2.64 g (63%) of 2b as a brown oil. ¹H NMR (300 MHz, CDCl₃) δ: 0.70–0.95 (m, 6H), 2.18 (s, 3H), 2.31 (s, 3H), 2.39 (s, 3H), 2.89–3.70 (br m, 4H), 6.94 (d, J = 7.2 Hz, 1H) 7.03 (s, 1H), 7.11–7.27 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ: 11.8, 13.6, 20.1, 21.1, 37.7, 42.2, 128.9, 130.2, 130.7, 136.9, 137.0, 170.4; HRMS (ESI-TOF) m/z [M+Na]⁺ for C₂₀H₂₅NO calcd 318.1828, found 318.1830. The data are in accordance with those previously reported (24).

**2-(2,3-dimethylphenyl)-N,N-diethyl-5-methylbenzamide (2d)**

A mixture of Pd(dppf) (0.386 g, 0.528 mmol) and 1-bromo-2,3-dimethylbenzene (1.96 g, 10.6 mmol) in DME (60 mL) was stirred at room temperature for 15 min before 1b (6.79 g, 21.1 mmol) in DME (40 mL) was added, followed by the addition of 2M aq. Na₂CO₃ (60 mL). Reaction and workup as described for 2a afforded 2.59 g (82%) of 2d as a brown oil. ¹H NMR (300 MHz, CDCl₃) δ: 0.67–0.95 (m, 6H), 2.07 (br s, 3H), 2.29 (d, 6H), 2.81–3.72 (br, 4H), 6.91–7.22 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ: 11.6, 13.5, 17.0, 20.4, 20.9, 37.6, 42.3, 128.8, 136.6, 136.8, 170.4, 120–140: several broad "hills"; IR (KBr, cm⁻¹): 1631, 1473, 1458, 1435, 826; HRMS (ESI-TOF) m/z [M+H]⁺ for C₂₀H₂₅NO calcd 296.20144, found 296.20168. Data deviate from those previously reported (24).
2,3-dimethylphenanthryl-6-trifluoromethanesulfonate (3a)
A stirred mixture of diisopropylamine (5.08 mL, 36.3 mmol) and n-BuLi (25.0 mL (1.45 M), 36.3 mmol) in anhydrous THF (85 mL) at 0°C was added 2a (4.28 g, 14.5 mmol). The mixture was stirred at room temperature for 30 min before being quenched with sat. aq. NH₄Cl (150 mL) and extracted with Et₂O (3 × 200 mL). The combined organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure. The crude 2,3-dimethyl-6-phenanthrol (14.5 mmol) and 2,6-lutidine (2.14 mL, 18.4 mmol) dissolved in DCM (50 mL) was stirred at 0°C for 5 min before addition of triflic anhydride (3.87 mL, 30 mL) as described for 3b. The mixture was stirred at room temperature for 30 min before being quenched with sat. aq. NH₄Cl (120 mL) and extracted with Et₂O (3 × 150 mL). The combined organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure. The crude 2,3-dimethyl-9-phenanthrol (8.48 mmol) and 2,6-lutidine (1.20 mL, 10.2 mmol) dissolved in DCM (130 mL) was stirred at 0°C for 5 min before addition of triflic anhydride (2.14 mL, 12.7 mmol). Reaction and workup as described for 3a afforded 2.15 g (71%) of 3b as a white powder. Mp = 138–139°C (Ethanol); ¹H NMR (300 MHz, CDCl₃) δ: 2.46 (s, 3H), 2.53 (s, 3H), 7.61–7.75 (m, 4H), 8.10 (d, J = 7.5 Hz, 1H), 8.39 (s, 1H), 8.65 (d, J = 7.5 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): 19.9, 20.6, 116.6, 120.9, 121.5, 122.8, 123.0, 125.0, 127.2, 127.8, 127.9, 128.8, 129.0, 131.5, 137.3, 137.5, 143.7; IR (KBr, cm⁻¹): 1415, 1218, 1143; HRMS (EI-TOF) m/z [M]+ for C₁₇H₁₃F₃OS calc 354.05375, found 354.05227.

2,7-dimethylphenanthryl-9-trifluoromethanesulfonate (3b)
A stirred mixture of diisopropylamine (2.97 mL, 21.2 mmol) and n-BuLi (18.6 mL (1.14 M), 21.2 mmol) in anhydrous THF (60 mL) at 0°C was added 2b (2.50 g, 8.48 mmol). The mixture was stirred at room temperature for 30 min before being quenched with sat. aq. NH₄Cl (120 mL) and extracted with Et₂O (3 × 150 mL). The combined organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure. The crude 2,7-dimethyl-9-phenanthrol (8.48 mmol) and 2,6-lutidine (1.20 mL, 10.2 mmol) dissolved in DCM (130 mL) was stirred at 0°C for 5 min before addition of triflic anhydride (2.14 mL, 12.7 mmol). Reaction and workup as described for 3a afforded 1.10 g (70%) of 3b as a white powder. 

2,6-dimethylphenanthryl-9-trifluoromethanesulfonate (3c)
A stirred mixture of diisopropylamine (1.55 mL, 11.1 mmol) and n-BuLi (10.8 mL, 11.1 mmol) in anhydrous THF (35 mL) at 0°C was added 2c (1.31 g, 4.44 mmol). The mixture was stirred at room temperature for 30 min before being quenched with sat. aq. NH₄Cl (40 mL) and extracted with Et₂O (3 × 40 mL). The combined organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure. The crude 2,6-dimethyl-9-phenanthrol (4.44 mmol) and 2,6-lutidine (0.63 mL, 5.33 mmol) dissolved in DCM (70 mL) was stirred at 0°C for 5 min before addition of triflic anhydride (1.12 mL, 6.67 mmol). Reaction and workup (water (10 mL), DCM (3 × 30 mL)) as described for 3a afforded 1.10 g (70%) of 3c as yellow solid. Mp = 83.5–84°C (Ethanol); ¹H NMR (300 MHz, CDCl₃) δ: 2.59 (s, 3H), 2.60 (s, 3H), 7.45 (dd, J = 8.1, 1.6 Hz, 1H), 7.56 (dd, J = 8.5, 1.8 Hz, 1H), 7.65 (s, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.88 (s, 1H), 8.38 (s, 1H), 8.56 (d, J = 8.5 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): 21.8, 22.1, 116.6, 117.7, 121.0, 122.3, 122.9, 125.6(C), 127.9(C), 128.7, 128.9, 129.4(C), 129.7, 137.7(C), 137.8(C), 143.6(C); IR (KBr, cm⁻¹): 1416, 1204, 1142, 914, 797, 608; HRMS (EI-TOF) [M]+ for C₁₇H₁₃F₃OS calc 354.05375, found 354.05236.

1,7-dimethylphenanthryl-9-trifluoromethanesulfonate (3d)
A stirred mixture of diisopropylamine (2.63 mL, 18.8 mmol) and n-BuLi (16.3 mL, 18.8 mmol) in anhydrous THF (60 mL) at 0°C was added 2d (2.23 g, 7.54 mmol). The mixture was stirred at room temperature for 30 min before being quenched with satd. aq. NH₄Cl (60 mL) and extracted with Et₂O (3 × 60 mL). The combined organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure. The crude 1,7-dimethyl-9-phenanthrol (7.537 mmol) and 2,6-lutidine (1.07 mL, 9.04 mmol)
dissolved in DCM (120 mL) was stirred at 0°C for 5 min before addition of triflic anhydride (1.90 mL, 11.3 mmol). Reaction and workup (water (20 mL), DCM (3 × 60 mL)) as described for 3a afforded 1.99 g (75%) of 3d as a white powder. Mp = 87–88°C (Ethanol, lit. 74–75°C [EtOAc]); 1H NMR (300 MHz, CDCl3) δ: 2.62 (s, 3H), 2.73 (s, 3H), 7.47 (d, J = 7.1 Hz, 1H), 7.56–7.62 (m, 2H), 7.90 (s, 1H), 7.91 (s, 1H), 8.51 (d, J = 8.4 Hz, 1H), 8.62 (d, J = 8.4 Hz, 1H); 13C NMR (75 MHz, CDCl3) δ: 19.7, 21.8, 114.3, 120.7, 121.0, 123.3, 127.4, 128.3, 130.0, 135.4, 137.8; IR (KBr, cm⁻¹): 1420, 1221, 1137, 784, 607; HRMS (EI-TOF) [M]+ C17H13F3O5S calc 354.05376 found 354.05243. 1H NMR data deviate in the two signals at 7.9 ppm from those previously reported (24). Most quaternary C were not detected.

2,3-dimethylphenanthrene (4a)

A reaction flask charged with 3a (3.43 g, 9.68 mmol), Pd(OAc)2 (40 mg, 0.19 mmol), PPh3 (0.101 g, 0.388 mmol), Et3N (4.06 mL, 29.088 mmol), and HCO2H (0.73 mL, 19.4 mmol) in DMF (190 mL) was stirred at 70°C for 30 min, before being cooled to room temperature, added water (190 mL) and extracted with Et2O (3 × 200 mL). The combined organic phase was dried over MgSO4 and concentrated under reduced pressure. The crude product was purified with flash column chromatography (5% EtOAc in PE) to afford 1.46 g (73%) of 4a as colorless crystals. Mp = 78.5–80°C (Ethanol, lit. 79–80°C [Ethanol] (28)); 1H NMR (300 MHz, CDCl3) δ: 2.26 (s, 3H), 2.52 (s, 3H), 7.51–7.65 (m, 5H), 7.84 (dm, J = 7.8 Hz, 1H), 8.43 (s, 1H), 8.62 (d, J = 8.4 Hz, 1H); 13C NMR (75 MHz, CDCl3) δ: 20.0, 20.6, 122.4, 122.9, 125.9(2CH), 126.2, 126.4, 128.5, 128.6, 130.0(C), 130.6(C), 131.8(C), 135.8(C), 135.9(C), one quaternary C was not detected; FTIR (KBr, cm⁻¹) 1445, 873, 808, 739, 710; HRMS (ESI-TOF) m/z [M]+ for C16H14; calcld. 206.10955, found 206.10456.

2,7-dimethylphenanthrene (4b)

A reaction flask charged with 3b (2.12 g, 5.98 mmol), Pd(OAc)2 (20 mg, 0.12 mmol), PPh3 (60 mg, 0.24 mmol), Et3N (2.50 mL, 18.0 mmol), and HCO2H (0.45 mL, 12.0 mmol) in DMF (120 mL) was stirred at 70°C for 30 min before being cooled to room temperature, added water (120 mL) and extracted with Et2O (3 × 200 mL). Workup as described for 4a afforded 1.17 g (94%) of 7b as colorless crystals. Mp = 101–102°C (Ethanol, lit. 101–102°C [Ethanol] (24)); 1H NMR (300 MHz, CDCl3) δ: 2.55 (s, 6H), 7.44 (dd, J = 8.4, 1.8 Hz, 2H), 7.64 (br s, 4H), 8.52 (d, J = 8.4 Hz, 2H); 13C NMR (75 MHz, CDCl3): 21.4, 122.3, 126.6, 128.0, 128.16(C), 128.22, 131.8(C), 135.8(C); IR (KBr, cm⁻¹): 1619, 1471, 1250, 890, 875, 815, 796, 708; HRMS (ESI-TOF) m/z [M+H]+ for C16H15; calcld. 207.1168, found 207.1165. NMR-data were in accordance with those previously reported (24).

2,6-dimethylphenanthrene (4c)

A reaction flask charged with 3c (1.01 g, 2.85 mmol), Pd(OAc)2 (13 mg, 0.057 mmol), PPh3 (30 mg, 0.11 mmol), Et3N (1.20 mL, 8.56 mmol), and HCO2H (0.23 mL, 5.7 mmol) in DMF (30 mL) was stirred at 70°C for 2 h, before being cooled to room temperature, added water (30 mL) and extracted with Et2O (3 × 30 mL). Workup as described for 4a afforded 574 mg (97%) of 4c as a brown liquid (lit Mp = 33–34°C [Methanol] (29)); 1H NMR (300 MHz, CDCl3) δ: 2.58 (s, 3H), 2.65 (s, 3H), 7.41 (dd, J = 8.1, 1.8 Hz, 1H), 7.47 (dd, J = 8.4, 1.8 Hz, 1H), 7.61–7.69 (m, 3H), 7.78 (d, J = 8.1 Hz, 1H), 8.46 (s, 1H), 8.58 (d, J = 8.4 Hz, 1H); 13C NMR (75 MHz, CDCl3) δ: 21.6, 22.3, 122.3, 122.6, 125.8, 126.8, 127.9, 128.0(C), 128.2(2CH), 128.5, 129.8(C), 130.5(C), 132.5(C), 136.2(C), 136.3(C); IR (KBr, cm⁻¹): 1621, 1458, 825, 478; HRMS (ESI-TOF) m/z [M]+ for C16H14; calcld. 206.10955, found 206.10613.

1,7-dimethylphenanthrene (4d)

A reaction flask charged with 3d (2.01 g, 5.67 mmol), Pd(OAc)2 (26 mg, 0.11 mmol), PPh3 (60 mg, 0.23 mmol), Et3N (2.37 mL, 17.0 mmol), and HCO2H (0.46 mL, 11.3 mmol) in DMF (60 mL) was stirred at 70°C for 2 h, before being cooled to room temperature, added water (60 mL) and extracted with Et2O (3 × 60 mL). Workup as described for 4a afforded 1.33 g (quant.) of 4d as a yellow solid. Mp = 78–80°C (Ethanol, lit 83–84°C [hexane] (24)); 1H NMR (400 MHz, CDCl3) δ: 2.56 (s, 3H), 2.75 (s, 3H), 7.41 (d, J = 7.1 Hz, 1H), 7.47 (dd, J = 8.5, 1.8 Hz, 1H), 7.52 (dd, J = 8.3, 7.2 Hz, 1H), 7.68 (s, 1H), 7.72 (d, J = 9.1 Hz, 1H), 7.93 (d, J = 9.1 Hz, 1H), 8.55 (d, J = 8.5 Hz, 1H), 8.59 (d, J = 8.5 Hz, 1H); 13C NMR (100 MHz,
CDCl$_3$ δ: 19.9, 21.4, 120.6, 122.8 (2CH), 126.0, 126.4, 127.3, 128.0, 128.3, 128.5 (C), 130.3 (C), 130.4 (C), 131.8 (C), 134.8 (C), 136.1 (C); IR (KBr, cm$^{-1}$): 1466, 1438, 1377, 1302, 1250, 881, 829, 792, 757; HRMS (EI-TOF) m/z [M]$^+$ for C$_{16}$H$_{14}$: calc 206.1095, found 206.10621. NMR-data were in accordance with those previously reported (24).

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