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Directed Metalation−Suzuki−Miyaura Cross-Coupling Strategies: Regioselective Synthesis of Hydroxylated 1-Methyl-phenanthrenes

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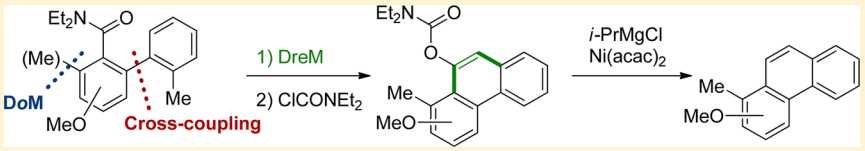
Supporting Information



ABSTRACT: A general, efficient, and regioselective synthesis of a series of hydroxylated 1-methylphenanthrenes **9** by a combined directed ortho metalation (DoM)−Suzuki−Miyaura cross-coupling−directed remote metalation (DreM) sequence is reported. Diversity to this methodology was achieved by a regioselective DoM rather than DreM reaction, affording more highly substituted phenanthrols (Table 2). Application of the turbo-Grignard reagent (*i*-PrMgCl·LiCl) in the Ni-catalyzed Corriu−Kumada reaction gave efficient decarbamoylation (Tables 3 and 4). Additional features are the TMS protecting group and halo-induced ipso-desilylation tactics applied to the regioselective synthesis of phenanthrenes (Scheme 2).

INTRODUCTION

The phenanthrene nucleus represents one of myriad ring systems of polycyclic aromatic hydrocarbons (PAHs)[1] and is present in large classes of natural products,[2] including a large group of alkaloids.[3] Substituted phenanthrenes have been exploited as antiviral[4] and anticancer agents,[5,6] fluorescent probes for DNA,[7] as antioxidant resveratrol analogues,[8] and in material science areas.[9] Unfortunately, phenanthrenes, as is the case for most classes of PAHs, are also persistent pollutants in the environment,[10,11] e.g., annelids on tidal flats concentrate phenanthrene in their excrements,[12] phenanthrene-based synthetic musk fragrances have been found in shrimps,[13] and metabolites of phenanthrenes have been detected in goat's milk.[14] Among the many fractions of PAHs in oil sources currently under study,[11,15] alkylated PAHs have been established to cause general detrimental environmental effects[10,16] and, in particular, are toxic to marine life.[17,18]

In the substantial body of literature on the construction of phenanthrenes,[19] the dominant classical Pschorr[20] and the more recent Mallory photo-[21] and oxidative cyclizations[22] have been augmented by an evolving number of transition metal-catalyzed methods,[6,16,23] including the popular Suzuki−Miyaura cross-coupling reaction.[24] Furthermore, phenanthrenes have been prepared from functionalized biphenyls by [4 + 2] benzannulation reactions[25] and by McMurry-like reactions.[26]

As part of our efforts to advance directed ortho metalation (DoM) reactions in aromatic and heteroaromatic synthesis,[27,28] we have devised combined metalation−cross-coupling strategies,[29] which have had particular relevance to the construction of phenanthrene derivatives.[30−32] In continuation of these efforts, we report herein a general route for the regioselective construction of 1-methyl-phenanthrenes bearing various positional hydroxy substituents by taking advantage of sequential DoM−Suzuki−Miyaura cross-coupling−directed remote metalation (DreM) reactions. Its retrosynthetic analysis is depicted in Scheme 1. In the penultimate step, the selective removal of the incipient 9-OH of the phenanthrol is carried out by transfer hydrogenation of the corresponding triflate or *β*-hydride-induced excision of the corresponding O-carbamate under Ni-catalyzed conditions, a procedure of considerable, as yet unfulfilled, promise.[33,34] In this work, we also advantageously adapted the silicon protection tactic for most reactive DoM sites[35,36] (A, Scheme 1) and the regioselective ipso-halodesilylation. Finally, we report on an apparent kinetic, thermodynamic ortho, remote metalation selectivity (B, Scheme 1) that allows the additional regioselective electrophile introduction into biaryl systems and thence leads to more highly substituted phenanthrenes.

RESULTS AND DISCUSSION

The results of Suzuki−Miyaura cross-coupling reactions of benzamides **1** with tolyl and xylyl derivatives **2** to give substituted biaryls **3** are summarized in Table 1. In many cases, both the cross-coupling of benzamide-derived boronic acid with halotoluene and the inverted reaction of halo benzamide with toluene-derived boronic acid were carried out to compare the efficiency of the respective routes. In addition, three different conditions were applied to establish generality. The boronic acid benzamides **1**, X = $B(OH)_2$, and bromobenzamides **1**, X = Br, were prepared by DoM reactions using standard procedures, whereas boronic acids **2**, Y = $B(OH)_2$, were obtained by metal−halogen exchange from the corresponding commercially available bromotoluenes followed by quench with a boron electrophile. Boronic acids **1a**, **1c**, and **1g** were prepared

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Scheme 1. Regioselective Synthesis of Substituted Phenanthrenes by the DoM−Cross-Coupling−DreM Strategy: Retrosynthetic Analysis

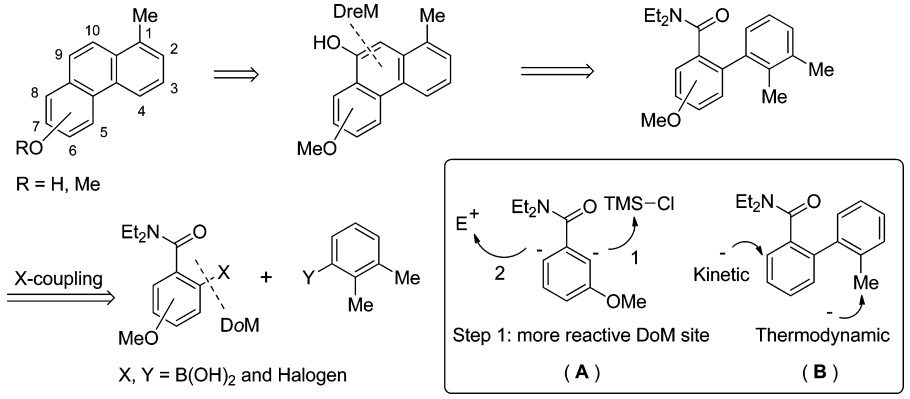
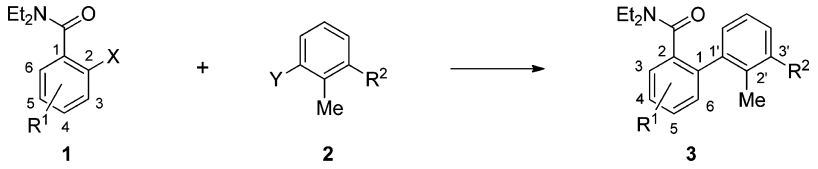


Table 1. Suzuki−Miyaura Cross-Coupling Route to Biaryl Amides 3a−3i



entry	compd.	X	R^1	compd.	Y	R^2	compd.	R^1	R^2	cond.[a]	yield[b] (%)
1	**1a**	$B(OH)_2$	H	**2a**	Br	H	**3a**	H	H	A	89
2	**1a**	$B(OH)_2$	H	**2b**	Br	Me	**3b**	H	Me	A	95
3	**1b**	Br	H	**2c**	$B(OH)_2$	H	**3a**	H	H	C	70−86
4	**1b**	Br	H	**2d**	$B(OH)_2$	Me	**3b**	H	Me	C	quant.
5	**1c**	$B(OH)_2$	6-OMe	**2b**	Br	Me	**3c**	3-OMe	Me	A	74
6	**1d**	$B(OH)_2$	3-OMe	**2b**	Br	Me	**3d**	6-OMe	Me	B	71
7	**1d**	$B(OH)_2$	3-OMe	**2e**	I	Me	**3d**	6-OMe	Me	A	47
8	**1e**	Br	3-OMe	**2c**	$B(OH)_2$	H	**3e**	6-OMe	H	B	73
9	**1f**	I	3-OMe	**2c**	$B(OH)_2$	H	**3e**	6-OMe	H	B	82−97
10	**1e**	Br	3-OMe	**2d**	$B(OH)_2$	Me	**3d**	6-OMe	Me	B	61−73
11	**1g**	$B(OH)_2$	4-OMe	**2a**	Br	H	**3f**	5-OMe	H	A	40
12	**1g**	$B(OH)_2$	4-OMe	**2b**	Br	Me	**3g**	5-OMe	Me	A	46
13	**1h**	Br	4-OMe	**2c**	$B(OH)_2$	H	**3f**	5-OMe	H	B	44
14	**1h**	Br	4-OMe	**2c**	$B(OH)_2$	H	**3f**	5-OMe	H	C	76−89
15	**1h**	Br	4-OMe	**2d**	$B(OH)_2$	Me	**3g**	5-OMe	Me	B	67
16	**1h**	Br	4-OMe	**2d**	$B(OH)_2$	Me	**3g**	5-OMe	Me	C	71
17	**1i**	$B(OH)_2$	5-OMe, 6-TMS	**2b**	Br	Me	**3h**	3-TMS, 4-OMe	Me	A	83
18	**1j**	Br	5-OMe, 6-TMS	**2c**	$B(OH)_2$	H	**3i**	3-TMS, 4-OMe	H	B	64
19	**1j**	Br	5-OMe, 6-TMS	**2c**	$B(OH)_2$	H	**3i**	3-TMS, 4-OMe	H	C	81
20	**1l**	I	5-OMe, 6-TMS	**2c**	$B(OH)_2$	H	**3i**	3-TMS, 4-OMe	H	C	95
30	**1f**	I	3-OMe	**2f**	$B(OH)_2$	H, 5-F	**3j**	6-OMe	H, 5′-F	B	75

[a]Conditions: (A) 3 mol % $Pd(PPh_3)_4$, DME/2 M Na_2CO_3, 100 °C, 18−20 h; (B) 5 mol % Pd_2dba_3, S-Phos, PhMe/K_3PO_4, 100 °C, 20−28 h; (C) 4 mol % Pd(dppf)Cl_2·DCM, dioxane/2 M K_2CO_3 (3/1), 90−100 °C, 16 h. [b]Yields of isolated products.

by using tri-isopropyl boronate, [B(*i*-OPr)$_3$] as the electrophile, which has the advantage of being more bench-stable than B(OMe)$_3$. However, the sterically hindered **1d** gave poor yields of product with B(*i*-OPr)$_3$ and therefore required the use of B(OMe)$_3$. This reaction was difficult to reproduce, requiring a careful quench at −40 °C to avoid decomposition of the product during workup.

Commercial bromotoluenes **2a** and **2b** conveniently served a double purpose since they were also used as cross-coupling partners. Two cases of an iodotoluene coupling reaction were tested (entries 7, 9). To comment briefly, cross-coupling of unsubstituted boronic acid benzamides with bromoarenes (entries 1, 2) or vice versa (entries 3, 4) under two different sets of conditions proceeded in high yields to give both monomethyl and dimethyl biaryls. A slightly buttressing influence of the 6-OMe group may be responsible for the lower yield (74%) of the biaryl product (entry 5). Interestingly, in moving from the 2,2′-substituted biaryl **3a**−**3c** to the considerably more hindered 2,2′,6-substituted series, **3d** and **3e**, the yields of products remained very good in both coupling partner combinations (entries 6−10).[37] The ^{1}H NMR spectra of all biphenyls indicated the presence of rotamers, which was more pronounced in the more crowded biphenyls.[38]

The cross-coupling reactions of the 4-OMe boronic acid benzamide and bromobenzamides series proved to be unexceptional, providing modest to good yields of biaryl products **3f**

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Scheme 2. Si Protection and ipso-Desilylation Routes to Benzamides 1e, 1f, 1j, and 1l

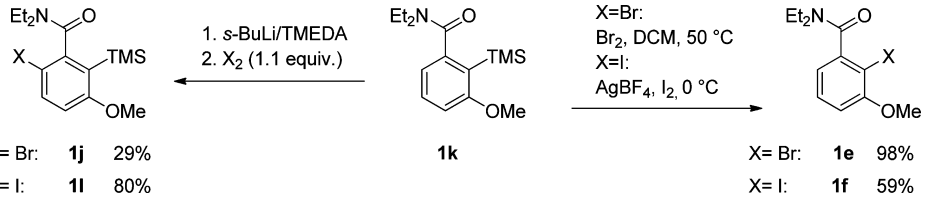
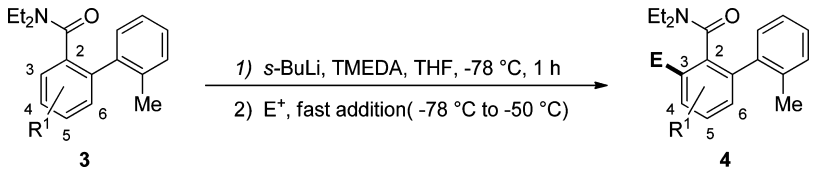


Table 2. DoM Reactions on Biaryl Amides 3: Synthesis of Compounds 4a−4f



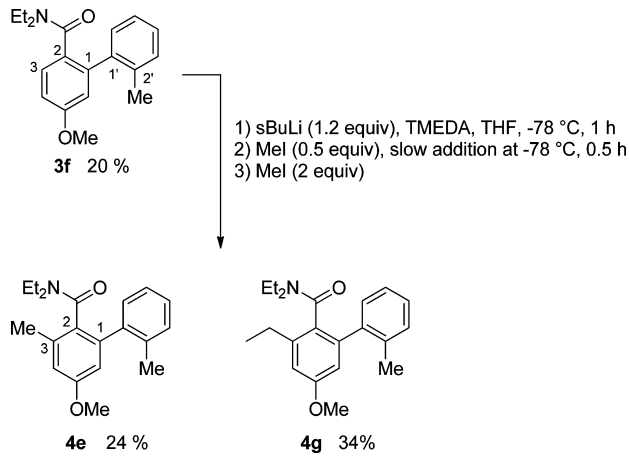
entry	compd.	R^1	E^+	product	E	yield[a] (%)
1	**3a**	H	MeI	**4a**	Me	85−95
2	**3a**	H	C_2Cl_6	**4b**	Cl	70
3	**3a**	H	TMSCl	**4c**	TMS	92
4	**3e**	6-OMe	MeI	**4d**	Me	78−82
5	**3f**	5-OMe	MeI	**4e**	Me	77−94
6	**3l**[b]	4-OMe	MeI	**4f**	Me	72−89

[a]Yields of isolated products. [b]Desilylation of **3i** (Table 1) with TBAF gave **3l** in 83% yield.

and **3g** (entries 11−16). While the 3-OMe benzamide 2-boronic acid **1d** was prepared by DoM chemistry using the less hindered $B(OMe)_3$ reagent, the corresponding halogenated products **1e**, **1f**, and **1h** were obtained via metalation and quench with Br_2 or I_2. Interestingly, using Br_2 as the electrophile seemed to consistently lead to poor yields in this approach (see also Scheme 2). Therefore, an alternative tactic was adopted, and both **1e** and **1f** were conveniently synthesized by the selective ipso-bromo and -iodo desilylation method[39] of the corresponding silylated derivative **1k** (Scheme 2), which was readily available on multigram scale. The requisite boronic acid and bromo derivatives **1i** and **1j** were obtained by DoM chemistry using the silicon protection of the most reactive metalation site method[35,36] followed by a second metalation and iodination or bromination. Cross-coupled products **3h** and **3i** were subsequently desilylated with TBAF into **3k** (Table 3) and **3l** (Table 2) in high yields for further use. The Suzuki−Miyaura coupling reaction of **1d** with iodo toluene **2e** proceeded in modest yields with $Pd(PPh_3)_4$ under aqueous conditions[31] and even less efficiently under anhydrous conditions (K_3PO_4/DMF) previously developed in our laboratories,[40] but it was considerably improved even in reactions with the bromotoluene **2b** using the Buchwald ligand SPhos under anhydrous conditions (entries 7 and 6).[37] Finally (entry 21), the fluorinated compound **2f** was coupled with **1f** to obtain biphenyl **3j** in good yields in order to extend the range of substituents.

In the course of the studies involving the conversion of the biaryl amides **3** into the corresponding phenanthrenes (Table 3), we observed the formation of products **4e** and **4g** under *s*-BuLi/TMEDA metalation and MeI quench conditions (Scheme 3). Formation of compound **4e** is expected by the kinetic C-3 deprotonation under the standard and widely used DoM *s*-BuLi/TMEDA conditions for tertiary amides,[28] whereas the formation of C-3 ethyl derivative **4g** is likely the result of an intermolecular C-3 anion (**3f**)−C-3 methyl (**4e**) proton exchange followed by methylation of the resulting tolyl anion.[41] The formation of **4g** is a function of the rate of addition of the MeI

Scheme 3. DoM Reaction of 3f and Slow Stepwise Quench with MeI



reagent, as expected since the incipient C-3 methyl anion is formed competitively with the original C-3 methylation.

The C-3 anion of **3f** was efficiently trapped to give **4e** in high yield by a procedure involving fast quench with neat MeI. In consideration of the potential value of this result for general substituted phenanthrene synthesis, it was generalized using two other electrophiles and for four biaryl substrates (Table 2), which does not require further comment.

With a series of biaryl amides in hand, the transformation to phenanthrols and eventually to the oxygenated 1-methyl phenanthrenes was undertaken, and the results are summarized in Table 3. Application of the standard LDA conditions of the DreM procedure[30,31] to the 2′,3′-dimethyl biaryl amide **3b** afforded the 1-methylphenanthren-9-ol **5a** in 68% yield of recrystallized material. The isomeric 3,2′-dimethyl biaryl amide **4a**, by treatment under the same LDA conditions, furnished the 8-methylphenanthren-9-ol **5b** in 89% yield of crude material. However, **5b** was significantly less stable than **5a** and partly

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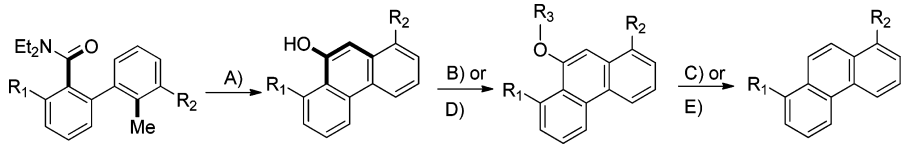
Table 3. Transformation of Biaryls 3 and 4 to Phenanthrenes 7



3 (R_1= H, R_2= Me)
4 (R_1= Me, R_2= H)

5

6 (R_3= $CONEt_2$ or Tf)

7

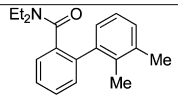
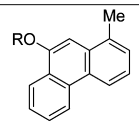
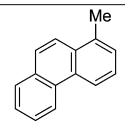
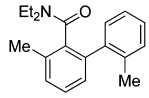
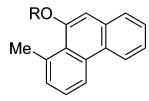
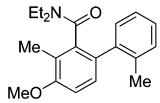
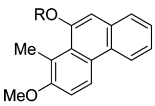
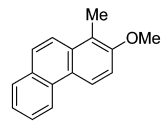
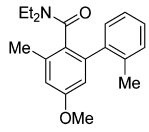
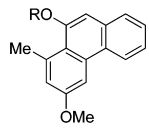
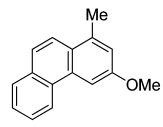
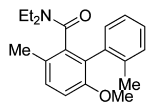
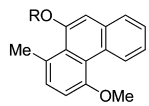
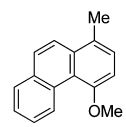
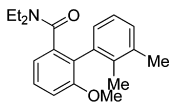
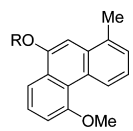
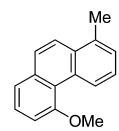
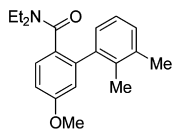
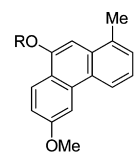
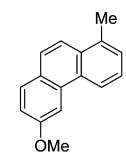
Entry	Biaryl	Cond.[a]	Phenanthrene	Yield (%)	Cond.[a]	Phenanthrene	Yield (%)[b]
							
1	**3b**	A	**5a** R = H	68			
2		A, B	**6a** R = $CONEt_2$	82	C	**7a**	97
							
3	**4a**	A	**5b** R = H	89[c]			
							
4	**4f**	A,D	**6b** R = Tf	55	E	**7b**	73
							
5	**4e**	A,B	**6c** R = $CONEt_2$	40-44	C	**7c**	75[e]
							
6	**4d**	A,B	**6d** R = $CONEt_2$	40-52	C	**7d**	88[e]
							
7	**3d**	A,B	**6e** R = $CONEt_2$	77			
8		A,D	**6f** R = Tf	92	E	**7e**	75
							

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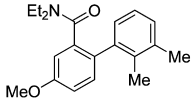
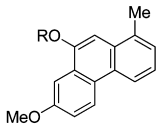
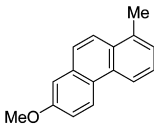
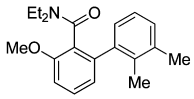
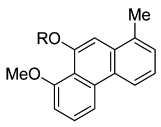
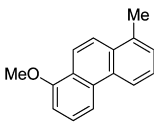
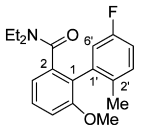
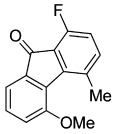
Table 3. continued

Entry	Biaryl	Cond.[a]	Phenanthrene		Yield (%)	Cond.[a]	Phenanthrene	Yield (%)[b]
9	**3g** 	A,B	**6g**	R = $CONEt_2$ 	74-77	C	**7f** 	83[e]
10	**3k**[d] 	A,B	**6h**	R = $CONEt_2$ 	92	C	**7g** 	79
11	**3c** 	A,B	**6i**	R = $CONEt_2$ 	81	C	**7h**	67
12	**3j**	A	**8**		79-97			65

[a]Conditions: (A) 2.5 equiv LDA, THF, 0 °C to rt; (B) (1) NaH, THF, 0 °C to rt, (2) $Et_2NC(O)Cl$; (C) 10% $Ni(acac)_2$, Et_2O, 2 equiv *i*-PrMgCl·LiCl in THF, rt; (D) CH_2Cl_2, pyridine (1.2 equiv), Tf_2O (1.2 equiv), rt, 8−12 h; (E) $Pd(OAc)_2$ (2 mol %), PPh_3 (4 mol %), Et_3N (3 equiv), DMF (10 mL/mmol), HCO_2H (2 equiv), 80 °C, 1 h. [b]Yields after flash chromatography. [c]Yield of crude product after extraction. The compound underwent rapid decomposition upon attempted purification by flash chromatography. [d]Desilylation of **3h** with TBAF gave **3k** in 94% yield (see Experimental Section). [e]The compound is contaminated with cross-coupled propyl and isopropyl group products. See Experimental Section for details.

decomposed during flash chromatography, and even Kugelrohr distillation, giving rapidly decreased yields upon purification. Therefore, rapid carbamoylation of the crude phenanthrols from the methoxy dimethyl biaryl benzamides **4e**, **4d**, **3d**, **3g**, **3k**, and **3c** was undertaken and directly furnished the corresponding phenanthrol O-carbamates **6c**−**6e** and **6g**−**6i**, respectively, without isolation of the respective phenanthrols, in modest to good yields. In two cases, the corresponding triflates (**6b** and **6f**) were also prepared. A study of the rotational barriers[38] of the starting biaryls may shed light upon the observed variations in yields. In this context, it is noted that the o-silylated amide **3h** required desilylation to **3k** before corresponding DreM reaction to **5i** could be achieved. The silylated derivative **3h** is expected to give the desilylated phenanthrylamine product.[42] Furthermore, in some cases, 2 equiv of LDA was required to effect the DreM transformation (e.g., **4d**, **4e**, and **4f**), as expected from the acidic C−H sites present in these molecules.

Finally, one unexpected DreM transformation not related to the major aim of this work, **3j** → **8** (entry 12), was observed. Although biphenyl 2-amides lacking a 2′-Me group are known to form fluorenones,[43] this represents, to our knowledge, the first example of a 2-amido-2′-Me biphenyl forming a fluorenone derivative under DreM conditions and suggests higher equilibrating acidity of C-6′ H over C-2′ methyl hydrogens under the LDA conditions. This result suggests an overriding DMG = F effect, as already established for DMG = OMe.[44]

For the generalization of the final reductive scission of the O-aryl carbamates **6** to the oxygenated 1-methylphenanthrenes **7**, an optimization study was carried out (Table 4). In the original work on the development of the Ni-catalyzed Kumada−Corriu cross-coupling reaction, Kumada had observed that Grignard reagents bearing *β*-hydrogens effect *β*-hydride transfer reactions and thereby reductive cleavage of aryl halides.[45,46] In our laboratories, we discovered this reaction for the O-carbamates.[33] In spite of the knowledge that the O-carbamate is the most powerful DMG and its promise in indole and scale-up chemistry,[33,47] this reaction remains broadly unexploited.[48]

Initial optimization studies on model compound **6a** (Table 4) using commercially available *i*-PrMgCl or *i*-PrMgCl·LiCl (turbo-Grignard)[49,50] failed in THF solution at 10 mol % $Ni(acac)_2$ loading (entry 1). However, in spite of using both reagents as THF solutions, reductive cleavage was observed in Et_2O as reaction solvent at room temperature. While *i*-PrMgCl produced mixtures of the desired decarbamoylated **7a**, together with the normal (**7i**) and isomeric (**7j**) Kumada−Corriu cross-coupled products[46] in varying amounts (entries 2 and 3), rapid injection of *i*-PrMgCl·LiCl afforded high ratios of **7a** to the two coupled products (entries 4 and 5). The *i*-PrMgCl·LiCl complex is considered to be more nucleophilic compared to *i*-PrMgCl,[50] and its use in a Grignard reaction has shown increased amounts of reduction products,[51] but, to our knowledge, this result constitutes the first intentional use of the turbo-Gringard reagent as a hydride source. For small-scale experiments, the higher 10 mol % catalyst loading is recommended to achieve fast completion of the reaction, although, as gleaned from the experiments, large-scale reactions should be feasible with low catalyst loading and thereby avoidance of environmental problems with excessive Ni

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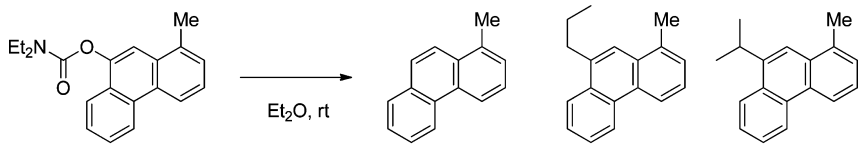
Table 4. Optimization of the Reductive O-Decarbamoylation of Compound 6a to 7a



6a **7a** **7i** **7j**

entry	Ni(acac)$_2$ (mol %)	Grignard[a]	equiv	time	product ratios (%)[b] 7a	7i	7j
1	10	*i*-PrMgCl·LiCl[c]	2	1.5 h	no reaction		
2	3	*i*-PrMgCl[d]	2	1 h	48	33	18
3	2	*i*-PrMgCl	4	4 h	77	14	8
4	10	*i*-PrMgCl·LiCl	2	15 min	98	2	0
5	1	*i*-PrMgCl·LiCl	2	22 h	97	2	1

[a]All Grignard reagents were commercial solutions in THF: *i*-PrMgCl (1 M) and *i*-PrMgCl·LiCl (14 w%). [b]Ratios of products by GC-MS analysis. [c]Reaction were carried out in THF. [d]Grignard reagent was added slowly (see Experimental Section).

residues. Although the cross-coupled products (**7i**, **7j**) were not isolated, they were readily identified on GC-MS by their main fragment from EI ionization arising from alkyl chain cleavages.

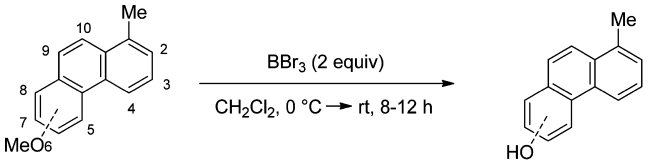
The optimized conditions were then applied to the phenanthrene O-carbamates **6a**, **6c**–**6e**, and **6g**–**6i** (Table 3, conditions C) to give good to quantitative yields of 1-methylphenanthrenes **7a**, **7c**, **7g**, and **7h**. Unfortunately, the reaction revealed its sensitivity, as compounds **7c**, **7d**, and **7f** contained significant amounts of cross-coupled products. Presumably, due to steric hindrance by a peri-type effect, **7h** was obtained in lower yield. In the case of triflates **6b** and **6f**, reductive cleavage by hydride transfer from formic acid (condition E)[30] gave products **7b** and **7e**, respectively. Although proceeding in very good yield, this method is less desirable due to its greater expense in the synthesis of the triflate **6f** compared to the O-carbamate derivative **6e**. In contrast, the byproducts formed in the reductive decarbamoylation route (cases **7i** and **7j**) were very difficult to separate from the desired phenanthrenes; therefore, the triflate procedure has merit when absolute purity is more important than cost.

To summarize, the reductive decarbamoylation completed the efficient regioselective synthesis of the series of ring A 2-, 3-, and 4-OMe 1-methylphenanthrenes as single isomers **7b**–**7d**. Furthermore, the synthetic "walking tour" of OMe groups provided the isomeric C-ring OMe-substituted 1-methylphenanthrenes **7e**–**7h** by the regioselective DoM–cross-coupling–DreM strategy. It is of interest to note that, although the further transformation of **5b** into the corresponding phenanthrene **7a** was not pursued, reductive excision of the OCONEt$_2$ group from the isomeric derivatives of **5a** (**6a**) and **5b** gives the same molecule. This observation is perhaps a conceptual element of broader utility in PAH synthesis and certainly of step economy value since **3b** is simpler to prepare than the isomeric **4a**.

As previously noted, phenanthrols are unstable to aerial oxidation to varying degrees. To conclude our study, reliable[52] BBr_3 deprotection[53] on three methoxy derivatives, **7f**, **7g**, and **7h**, was carried out to afford the corresponding phenols **9c**, **9b**, and **9a**, respectively (Scheme 4), in order to demonstrate the relative higher stability of non 9-hydroxy phenanthrenes and the ability to make such products available as standards for PAH environmental and metabolism studies.[17]

In summary, we have provided a systematic study of a general, efficient, and regioselective synthesis of phenanthrenes that allows this class of PAHs to be prepared with minimal handling

Scheme 4. Demethylation of 1-Methylphenanthrenes 7 to Phenanthrols 9



7h	(8-OMe)	8-Methylphenanthren-1-ol	**9a**	57%
7g	(7-OMe)	8-Methylphenanthren-2-ol	**9b**	94%
7f	(6-OMe)	8-Methylphenanthren-3-ol	**9c**	87%

of potentially carcinogenic materials and without using Lewis acid and other powerful reagents and harsh conditions. The route involves application of the combined DoM–Suzuki–Miyaura cross-coupling–DreM strategy to give a significant number of phenanthrenes (Tables 1 and 3) via the intermediate phenanthrols, which are subjected to conversion to the corresponding triflates and O-carbamates followed by Ni-catalyzed scission. In addition, previously developed silicon protecting group and ipso-desilylation reactions have been applied (Scheme 2) and a new DoM over DreM reaction of 2-amido-2′-methyl biphenyls has been uncovered (Table 2) that invite further application in aromatic synthesis.

EXPERIMENTAL SECTION

General Methods. Melting points were measured in capillary tubes and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on 400 or 500 MHz spectrometers. The chemical shifts of ^{1}H and ^{13}C NMR signals are quoted relative to internal C*H*Cl$_3$ (δ = 7.26) and C*D*Cl$_3$ (δ = 77.0), DMSO-d_6 (δ = 2.50 and 45.0), acetone-d_6 (δ = 2.05 and 29.8/206.3), or tetramethylsilane (δ = 0.0). ^{1}H NMR data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet, etc.), coupling constant (Hz), and relative intensity. ^{13}C NMR data are reported as follows: chemical shift in ppm (δ). The GC-MS analyses were performed under EI conditions. High-resolution mass spectra were obtained on a EI or ESI time-of-flight mass spectrometer. All reactions involving alkyllithiums were carried out under argon in flame-dried glassware, using syringe-septum cap techniques. Anhydrous THF and Et$_2$O were obtained by treatment using solvent purification system with final drying through molecular sieves under argon. All purchased chemicals were used without further purification. Alkyllithiums were titrated before use.[54] Flash column chromatography was carried out using silica gel (particle size: 40–60 μm, 60A).

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General Synthetic Procedures. The starting benzamides (*N*,*N*-diethyl-2-methoxybenzamide, *N*,*N*-diethyl-3-methoxybenzamide, *N*,*N*-diethyl-4-methoxybenzamide, and **1b**) were synthesized from the corresponding benzoic acids using $SOCl_2$ and $HNEt_2$,[55] and the spectral and analytical data of the products matched those that have been reported.[56]

The benzamide boronic acids **1a**, **1c**, **1d**, **1g**, and **1i** were synthesized according to general procedure A and were used directly without further purification. The synthesis and subsequent cross-coupling of compound **1d** was difficult to reproduce, despite the care taken to avoid decomposition.

ortho-Tolyl (**2c**) and -xylyl (**2d**) boronic acids as well as 5-fluoro-2-methylbenzene boronic acid (**2f**) were purchased from Sigma-Aldrich, as were the corresponding bromides and iodides (**2a**, **2b**, **2e**).

Compounds **3a**, **3f**, **3e** were synthesized as reported,[30] as were compounds **3b**, **5a**, and **7a**.[31]

The more highly substituted biaryls exhibited rotamers, resulting in ^{1}H NMR spectra that were not well-defined. For some biaryls, VT NMR studies in DMSO solution indicated coalescence of certain peaks, and for some biaryls, not all of the carbon peaks were observed in the ^{13}C NMR.

For the synthesis of some final phenanthrenes, the Ni-catalyzed decarbamoylation reaction leads to linear and rearranged *i*-PrMgCl coupling rather than decarbamoylation. In some cases, it was not possible to fully eradicate this impurity from the desired product, and these are indicated where relevant.

General Procedure: Directed Ortho Metalation (A). To a solution of TMEDA (1.0−2.2 equiv) in THF (5−10 mL/mmol) cooled to 0 °C was added a solution of *s*-BuLi (1.0−2.2 equiv), and the mixture was cooled to −78 °C. The starting material (1.0 equiv) in THF (5−10 mL/mmol) was added dropwise while keeping the internal temperature below −70 °C. The reaction mixture was stirred for 1 h, or the time indicated in the specific procedure, and then the electrophile was added, either neat or as a solution in THF. The cooling bath was removed, and the reaction mixture was warmed to room temperature. Saturated solution of NH_4Cl was added (10 mL/mmol), and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The organic layers were combined, dried ($MgSO_4$), and evaporated to dryness. The residue was purified via column chromatography.

General Procedure: Directed Remote Metalation (B). Under argon, LDA in THF (1.1−2.5 equiv) was either prepared at 0 °C using *n*-BuLi (1.1−2.5 equiv) and diisopropylamine [DIPA] (1.1−2.5 equiv) in THF (10−30 mL/mmol) or commercial LDA solution (2.0 M in ethylbenzene/THF/heptane, 1.1−2.5 equiv) was utilized. The starting material (1.0 equiv) was dissolved in dry THF (5−10 mL/mmol) and added to the LDA solution dropwise at −20 to 0 °C. The solution was stirred for 4−24 h and quenched with saturated NH_4Cl solution (20 mL/mmol). The mixture was extracted with CH_2Cl_2 (3 × 20 mL), dried ($MgSO_4$), and evaporated to dryness in vacuo. The residue was purified via column chromatography or taken directly onto the next step.

General Procedure: Cross-Coupling I (C). The starting halide (1.0 equiv) and the boronic acid (1.2−2.0 equiv) were dissolved in degassed dioxane/2 M aqueous K_2CO_3 mixture (10 mL dioxane/mmol substrate; 4−6 equiv K_2CO_3). To this solution was added $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ complex (4−5 mol %), and the mixture was immersed into a preheated oil bath at 90−100 °C and maintained at this temperature for 16 h. Water (10 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The organic layers were dried ($MgSO_4$) and evaporated to dryness. The residue was purified by column chromatography.

General Procedure: Cross-Coupling II (D). The starting halide (1.0 equiv) and boronic acid (1.1−1.5 equiv) were dissolved in toluene (7−10 mL/mmol) and degassed for 5−10 min by bubbling argon through the solution. K_3PO_4 (4.0−5.0 equiv) was added, followed by Pd_2dba_3 (2−3 mol %) and SPhos (5−10 mol %). The reaction mixture was immersed in a preheated oil bath at 110 °C, and the temperature was maintained overnight. The reaction mixture was filtered and washed with EtOAc, and after evaporation, the residue was purified via column chromatography.

General Procedure: Cross-Coupling III (E). The starting halide (1.0 equiv) and the boronic acid (1.2−2.5 equiv) were dissolved in degassed dimethoxyethane and 2 M aqueous Na_2CO_3 mixture (7−10 mL dimethoxyethane/mmol substrate; 4−6 equiv Na_2CO_3). To this solution was added $Pd(PPh_3)_4$ (3−5 mol %), and the solution was maintained at reflux temperature overnight (16 h). The mixture was extracted with diethyl ether (3 × 10 mL/mmol substrate). Organic layers were dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography.

General Procedure: Desilylation (F). The starting biaryl (1.0 equiv) was dissolved in dry THF (5−10 mL/mmol), and TBAF was added (1 M in THF, 2−3 equiv). After the reaction was complete according to TLC (2−16 h), the solvent was evaporated. The residue was purified via column chromatography.

General Procedure: Detriflation (G). The starting triflate (1.0 equiv) was dissolved in DMF (10 mL/mmol), and the mixture was degassed by bubbling argon with a needle for 5−10 min. Then, Et_3N (3.0 equiv), HCO_2H (2.0 equiv), $PdOAc_2$ (2 mol %), and PPh_3 (4 mol %) were added. The mixture was placed in a preheated oil bath at 80 °C for 1 h. The mixture was cooled to rt, H_2O (15 mL/mmol) was added, and the mixture was extracted with CH_2Cl_2 (2 × 20 mL). After evaporating to dryness, the residue was purified via column chromatography.

General Procedure: Decarbamoylation (H). The starting material (1 equiv) was dissolved in dry Et_2O (20 mL/mmol), and $Ni(acac)_2$ (10 mol %) was added. The suspension was cooled to 0 °C, and *i*-PrMgCl·LiCl (2.5 equiv, solution in THF) was added. The mixture was allowed to warm to room temperature overnight. Then, H_2O (20 mL/mmol) was added, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined organics were dried ($MgSO_4$) and evaporated. The residue was purified via column chromatography.

General Procedure: BBr_3 Demethylation (I). The phenanthrene was dissolved in dry CH_2Cl_2 (50 mL/mmol). The solution was cooled to 0 °C, and BBr_3 (2.0 equiv) was added dropwise. The ice bath was removed, and the mixture was stirred at room temperature overnight. Water (20 mL) was added, and the organic layer was separated. The aqueous layer was additionally extracted with CH_2Cl_2 (2 × 20 mL). The organic layers were combined and dried ($MgSO_4$), and after evaporation, the residue was purified via column chromatography.

***N*,*N*-Diethyl-2-bromo-3-methoxy-benzamide (1e).** The title compound was synthesized by dissolving **1k** (2.50 g, 8.95 mmol, 1.0 equiv) in CCl_4 (50 mL). At 0 °C, Br_2 (483 μL, 9.39 mmol, 1.05 equiv) was added, and the mixture was warmed to 50 °C for 2 h. After cooling to room temperature, the solution was evaporated and the residue was subjected to column chromatography using pentane/Et_2O (1:1 to 0:1 gradient). The title compound was isolated as a colorless oil (2.5 g, 98%). Physical and spectral data are in agreement with those reported.[57]

***N*,*N*-Diethyl-2-iodo-3-methoxy-benzamide (1f).** The title compound was synthesized by dissolving **1k** (280 mg, 1.0 mmol, 1.0 equiv) in MeOH (10 mL) and adding $AgBF_4$ (202 mg, 1.1 mmol, 1.1 equiv). At 0 °C, I_2 (305 mg, 1.2 mmol, 1.2 equiv) was added, and the mixture was warmed to room temperature and stirred at this temperature overnight. The next day, EtOAc was added (20 mL), and the suspension was filtered and evaporated to dryness. EtOAc (50 mL) was added, and the suspension washed with 2 M HCl (10 mL) and H_2O (20 mL). The organic layer was dried ($MgSO_4$) and evaporated, and the residue was subjected to column chromatography using hexanes/EtOAc (2:1 to 1:1 gradient). The title compound was isolated as a colorless oil (197 mg, 59%). ^{1}H NMR data are similar to those reported but obtained in C_6D_6.[58] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, J = 7.9 Hz, 1H), 6.80 (dd, J = 1.0, 7.5 Hz, 1H), 6.77 (dd, J = 1.0, 8.2 Hz, 1H), 3.88 (s, 3H), 3.80−3.90 (m, 1H), 3.22−3.34 (m, 1H), 3.02−3.19 (m, 2H), 1.28 (t, J = 7.2 Hz, 3H), 1.05 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.4, 13.8, 38.8, 42.6, 56.5, 85.1, 110.3, 119.1, 129.8, 144.7, 158.2, 169.9; MS (EI, DIP) m/z 333 (M^+, 61), 332 (56), 261 (100), 218 (15), 206 (34), 195 (30), 165 (19), 135 (19); FTIR (neat, cm^{-1}) 2972, 2934, 1628, 1562, 1424, 1296, 1262, 1053, 786; HRMS (EI-TOF) m/z $[M]^+$ for $C_{12}H_{16}INO_2$: calcd, 333.0226; found, 333.0215.

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***N,N*-Diethyl-2-bromo-4-methoxy-benzamide (1h).** The title compound was synthesized according to general procedure A using TMEDA (1.52 mL, 10.13 mmol, 1.05 equiv), *s*-BuLi (1.33 M in cyclohexane, 7.62 mL, 10.13 mmol, 1.05 equiv) in THF (25 mL), *N,N*-diethyl-4-methoxybenzamide (2.00 g, 9.65 mmol, 1.0 equiv) in THF (5 mL), and Br_2 (522 μL, 10.13 mmol, 1.05 equiv). After standard workup, with an additional wash with sodium thiosulfate (sat., 20 mL), the residue was purified via column chromatography using CH_2Cl_2/Et_2O (10:0 to 10:1 gradient). The title compound was isolated as a colorless oil (1.19 g, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 8.5 Hz, 1H), 7.08 (d, J = 2.4 Hz, 1H), 6.86 (dd, J = 2.4, 8.5 Hz, 1H), 3.79 (s, 4H [-OCH_3 + -NCH]), 3.32 (br s, 1H), 3.14 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H), 1.04 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.5, 13.9, 39.0, 42.7, 55.5, 113.6, 117.9, 119.8, 128.2, 131.1, 160.0, 168.5; MS (EI, DIP) m/z 286/284 (M^+, 20), 215/213 (100), 172/170 (15), 135 (26); FTIR (KBr, cm^{-1}) 2973, 2935, 1633, 1601, 1564, 1469, 1427, 1288, 1195, 1032, 884; HRMS (ESI-TOF) m/z $[M + H]^+$ for $C_{12}H_{17}BrNO_2$: calcd, 286.0443; found, 286.0442.

***N,N*-Diethyl-6-bromo-3-methoxy-2-trimethylsilyl-benzamide (1j).** The title compound was synthesized according to general procedure A using TMEDA (650 μL, 4.31 mmol, 1.2 equiv), *s*-BuLi (1.35 M in cyclohexane, 3.18 mL, 4.31 mmol, 1.2 equiv) in THF (20 mL), **1k** (1.0 g, 3.58 mmol, 1.0 equiv) in THF (5 mL), and Br_2 (202 μL, 3.93 mmol, 1.1 equiv) in THF (5 mL). After standard workup, with an additional wash with sodium thiosulfate (sat., 20 mL), the residue was purified via column chromatography using pentane/Et_2O (5:1 to 3:1 gradient). The title compound was isolated as a colorless oil that solidifies on standing (375 mg, 29%). mp 99−100 °C (hexanes/Et_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.8 Hz, 1H), 6.67 (d, J = 8.8 Hz, 1H), 3.91 (sex, J = 6.6 Hz, 1H), 3.77 (s, 3H), 3.01−3.27 (m, 3H), 1.26 (t, J = 7.2 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H), 0.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.3, 12.0, 13.1, 38.7, 42.8, 55.3, 111.3, 111.4, 127.3, 134.5, 143.7, 163.9, 168.5; MS (EI, DIP) m/z 359/357 (M^+, 7), 344/342 (100), 287/285 (9), 219 (29); FTIR (KBr, cm^{-1}) 2975, 1639, 1461, 1413, 1380, 1286, 1244, 1057, 846; HRMS (EI-TOF) m/z $[M]^+$ for $C_{15}H_{24}BrNO_2Si$: calcd, 357.0760; found, 357.0759.

***N,N*-Diethyl-3-methoxy-2-trimethylsilylbenzamide (1k).** The title compound was synthesized according to general procedure A using TMEDA (1.65 mL, 11.0 mmol, 1.1 equiv), *s*-BuLi (1.4 M in cyclohexane, 7.5 mL, 10.5 mmol, 1.05 equiv) in THF (25 mL), *N,N*-diethyl-3-methoxybenzamide (2.07 g, 10.0 mmol, 1.0 equiv) in THF (10 mL), and TMSCl (4.0 mL, 31.5 mmol, 3.15 equiv). After standard workup, the residue was purified via column chromatography using pentane/Et_2O (5:1 to 3:1 to 1:1 gradient). The title compound was isolated as a pale yellow solid (2.12 g, 76%). mp 51−52 °C (hexanes, lit. 54−55 °C [hexanes]);[36] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, J = 8.1 Hz, 1H), 6.80 (d, J = 8.3 Hz, 1H), 6.73 (d, J = 7.5 Hz, 1H), 3.79 (s, 3H), 3.61 (br s, 1H), 3.40 (br s, 1H), 3.21 (br s, 1H), 3.13 (br s, 1H), 1.24 (t, J = 7.2 Hz, 3H), 1.05 (t, J = 7.2 Hz, 3H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.4, 12.7, 13.6, 38.9, 43.3, 55.1, 109.7, 118.8, 124.3, 130.4, 144.5, 164.8, 171.7.

***N,N*-Diethyl-6-iodo-3-methoxy-2-trimethylsilyl-benzamide (1l).** The title compound was synthesized according to general procedure A using TMEDA (335 μL, 2.23 mmol, 1.3 equiv), *s*-BuLi (1.4 M in cyclohexane, 1.5 mL, 2.1 mmol, 1.2 equiv) in THF (10 mL), **1k** (480 mg, 1.72 mmol, 1.0 equiv) in THF (10 mL), and I_2 (570 mg, 2.25 mmol, 1.3 equiv) in THF (2 mL). After standard workup, with an additional wash with sodium thiosulfate (sat., 20 mL), the residue was purified via column chromatography using pentane/Et_2O (5:1 to 3:1 gradient). The title compound was isolated as a colorless solid (556 mg, 80%). mp 108−109 °C (Et_2O, lit. 100−101 °C [hexanes]);[36] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.7 Hz, 1H), 6.55 (d, J = 8.7 Hz, 1H), 3.93 (sex, J = 6.7 Hz, 1H), 3.78 (s, 3H), 3.01−3.27 (m, 3H), 1.30 (t, J = 7.2 Hz, 3H), 1.11 (t, J = 7.2 Hz, 3H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.4, 12.0, 13.1, 38.9, 43.0, 55.3, 84.3, 111.8, 127.5, 141.2, 147.5, 164.8, 170.1.

***N,N*-Diethyl-2′-methylbiphenyl-2-carboxamide (3a).** The title compound was synthesized according to general procedure E using **1a** (2.42 g, 10.9 mmol, 1.4 equiv), **2a** (1.21 g, 7.1 mmol, 1.0 equiv), 2 M aqueous K_2CO_3 (20 mL, 40.00 mmol, 5.6 equiv), and $Pd(PPh_3)_4$ (246 mg, 0.213 mmol, 3.0 mol %) in 35 mL of dimethoxyethane and 5 mL ethanol. After standard workup, the residue was purified via column chromatography using heptane/Ethyl acetate (2:1) to afford the title product as a colorless oil that solidifies (1.74 g, 89% yield). mp 65−66.5 °C (cyclohexane, lit. 67−68 °C [hexanes][30]); ^{1}H NMR (400 MHz, DMSO-d_6, 70 °C) δ 7.36−7.48 (m, 2H), 7.28−7.35 (m, 1H), 7.18−7.28 (m, 3H), 7.05−7.17 (m, 2H), 3.18 (br s, 2H), 2.93 (br s, 2H), 2.13 (s, 3H), 0.88 (br s, 3H), 0.67 (br s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 12.2, 14.0, 20.4, 37.9, 42.5, 125.4, 126.6, 127.7, 128.0, 128.6, 129.9, 130.3, 130.5, 136.2, 137.8, 138.3, 139.7, 169.4; MS (EI, DIP) m/z 267 (M^+, 22), 266 (22), 195 (M^+, 100), 167 (40), 165 (69), 152 (45); FTIR (KBr, cm^{-1}) 2965, 1631, 1428, 755; HRMS (EI-TOF) m/z $[M]^+$ for $C_{18}H_{21}NO$: calcd, 267.1623; found, 267.1635.

***N,N*-Diethyl-3-methoxy-2′,3′-dimethylbiphenyl-2-carboxamide (3c).** Compound **1c** was synthesized according to general procedure A using TMEDA (2.7 mL, 18.0 mmol, 1.20 equiv), *s*-BuLi (1.23 M in cyclohexane, 14.6 mL, 18.0 mmol, 1.20 equiv) in THF (30 mL), *N,N*-diethyl-2-methoxybenzamide (3.1 g, 15.0 mmol, 1.0 equiv) in THF (30 mL), and tri*iso*propylborate (8.3 mL, 36 mmol, 2.4 equiv). After standard workup (quench with sat. aq. NH_4Cl and ether extraction), crude **1c** (3.94 g, 104%) was isolated and used in the next step without further purification.

The title compound **3c** was synthesized according to general procedure E using **1c** (3.94 g, 15 mmol, 1.5 equiv), **2b** (1.83 g, 9.89 mmol, 1.00 equiv), 2 M aqueous Na_2CO_3 (40 mL), and $Pd(PPh_3)_4$ (347 mg, 0.3 mmol, 3.0 mol %) in 40 mL of dimethoxyethane. After standard workup, the residue was purified via column chromatography using heptane/ethyl acetate (2:1) to afford the title product as a colorless oil that solidifies (2.28 g, 74% yield). mp 123−124 °C (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two rotamers: major (A) and minor (B)) δ 7.26−7.38 (A + B, m, 3H), 7.03−7.14 (A + B, m, 3H), 7.00 (B, t, J = 7.5 Hz, 1H), 6.88−6.94 (A + B, m, 2H), 6.85 (A, d, J = 4.2 Hz, 1H), 6.84 (B, d, J = 4.4 Hz, 1H), 6.79 (B, d, J = 7.6 Hz, 1H), 3.86 (B, s, 3H), 3.85 (A, s, 3H), 3.78 (A + B, sex, J = 6.8 Hz, 2H), 3.26 (A, sex, J = 7.1 Hz, 1H), 3.10 (B, sex, J = 7.0 Hz, 1H), 2.65−2.97 (A + B, m, 4H), 2.28 (B, s, 3H), 2.27 (A, s, 3H), 2.08 (B, s, 3H), 2.06 (A, s, 3H), 1.03 (A, t, J = 7.1 Hz, 3H), 0.88 (B, t, J = 7.1 Hz, 3H), 0.52−0.67 (A + B, m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.5, 11.6, 13.5, 13.5, 17.0, 17.3, 20.4, 20.5, 37.3, 37.5, 42.1, 42.4, 55.3, 55.6, 109.2, 109.3, 122.0, 123.2, 124.0, 124.9, 125.8, 126.0, 126.4, 128.3, 128.8, 128.9, 128.9, 129.0, 133.2, 136.0, 136.4, 136.8, 138.3, 139.4, 139.7, 141.1, 155.2, 155.9, 167.2, 167.4; MS (EI, DIP) m/z 311 (M^+, 2), 280 (2), 239 (100), 224 (7), 196 (10), 181 (7), 165 (12), 152 (8); FTIR (KBr, cm-1) 2980, 2930, 1627, 1461, 1285, 1256, 1067; HRMS (EI-TOF) m/z $[M]^+$ for $C_{20}H_{25}NO_2$: calcd, 311.1885; found, 311.1879.

***N,N*-Diethyl-6-methoxy-2′,3′-dimethylbiphenyl-2-carboxamide (3d).** The title compound was synthesized according to general procedure D using **1e** (400 mg, 1.40 mmol, 1.0 equiv), **2d** (300 mg, 2.00 mmol, 1.4 equiv), K_3PO_4 (1.40 g, 6.60 mmol, 4.7 equiv), Pd_2dba_3 (32 mg, 0.035 mmol, 2.5 mol %), and SPhos (32 mg, 0.080 mmol, 5.7 mol %) in 10 mL of toluene. After standard workup, the residue was purified via column chromatography using hexanes/EtOAc (3:1 to 1:1 gradient) to afford the title product as a colorless oil (310 mg, 71% yield). ^{1}H NMR (400 MHz, 70 °C, DMSO-d_6) δ 7.40 (t, J = 7.9 Hz, 1H), 7.09 (t, J = 8.4 Hz, 2H), 6.99 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 7.4 Hz, 2H), 3.70 (s, 3H), 2.75−3.30 (m, 4H), 2.25 (s, 3H), 1.93 (s, 3H), 0.91 (br s, 3H), 0.61 (br s, 3H); ^{13}C NMR (100 MHz, 70 °C, DMSO-d_6) δ 11.0, 13.0, 15.8, 19.4, 36.6, 41.4, 55.1, 110.7, 117.3, 123.7, 126.8, 128.1 (2C), 134.9, 138.4, 156.1, 167.9; MS (EI, DIP) m/z 311 (M^+, 29), 239 (83), 238 (100), 224 (24), 209 (6), 195 (11), 181 (13), 165 (16), 152 (13); FTIR (KBr, cm^{-1}) 2970, 2931, 1634, 1457, 1427, 1314, 1296, 1059; HRMS (EI-TOF) m/z $[M - H]^+$ for $C_{20}H_{24}NO_2$: calcd, 310.1807; found, 310.1795.

***N,N*-Diethyl-6-methoxy-2′-methylbiphenyl-2-carboxamide (3e).** The title compound was synthesized according to general procedure D using **1f** (1.44 g, 4.08 mmol, 1.0 equiv), **2c** (832 mg, 6.11 mmol, 1.5 equiv), K_3PO_4 (3.46 g, 16.30 mmol, 4.0 equiv), Pd_2dba_3 (85 mg,

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0.093 mmol, 2.3 mol %), and SPhos (135 mg, 0.33 mmol, 8.0 mol %) in 35 mL of toluene. After standard workup, the residue was purified via column chromatography using pentane/Et_2O (1:1) to afford the title product as a colorless oil that solidifies (1.01 g, 82% yield). Physical and spectral data are in agreement with those reported.[30] mp 110.5−112.5 °C (hexanes/Et_2O, lit. 105−107 °C [hexane][30]); ^{1}H NMR (400 MHz, DMSO-d_6, 70 °C) δ 7.41 (t, J = 8.0 Hz, 1H), 7.15−7.22 (m, 2H), 7.11 (d, J = 8.2 Hz, 1H), 6.98−7.06 (m, 1H), 6.88 (d, J = 7.5 Hz, 1H), 3.71 (s, 3H), 2.70−3.35 (m, 4H), 2.04 (s, 3H), 0.93 (br s, 3H), 0.61 (t, J = 6.0 Hz, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6, 70 °C) δ 12.1, 14.0, 20.0, 37.6, 42.4, 56.2, 111.8, 118.3, 125.2, 127.7, 129.3, 129.6, 135.9, 137.6, 139.4, 157.1, 168.9; FTIR (KBr, cm^{-1}) 2971, 2932, 1632, 1460, 1427, 1296, 1256, 1059; MS (EI, DIP) m/z 297 (M$^+$, 48), 225 (100), 224 (90), 210 (45), 181 (27), 166 (42), 152 (29), 84 (55); HRMS (EI-TOF) m/z [M]$^+$ for $C_{19}H_{23}NO_2$: calcd, 297.1729; found, 297.1718.

***N,N*-Diethyl-5-methoxy-2′,3′-dimethylbiphenyl-2-carboxamide (3g).** The title compound was synthesized according to general procedure C using **1h** (143 mg, 0.50 mmol, 1.0 equiv), **2d** (225 mg, 1.50 mmol, 3.0 equiv), 2 M aqueous K_2CO_3 (1.5 mL, 3.00 mmol, 6.0 equiv), and Pd(dppf)Cl_2·CH_2Cl_2 (20 mg, 0.024 mmol, 4.9 mol %) in 5 mL of dioxane. After standard workup, the residue was purified via column chromatography using hexanes/EtOAc (9:1 to 5:1 gradient) to afford the title product as a colorless oil (110 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$; one aromatic proton exhibits a very broad peak and is visible only when the spectrum intensity is increased) δ 7.29 (d, J = 8.3 Hz, 1H), 7.11 (d, J = 8.6 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.92 (dd, J = 2.5, 8.4 Hz, 1H), 6.76 (d, J = 2.5 Hz, 1H), 3.82 (s, 3H), 2.40−3.75 (m, 4H), 2.29 (s, 3H), 2.11 (s, 3H), 0.89 (br s, 3H), 0.67 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7, 13.7, 17.1, 20.5, 37.9, 42.5, 55.3, 112.7, 115.5, 124.6, 127.5, 129.1, 129.7, 136.9, 159.1, 170.2 MS (EI, DIP) m/z 311 (M$^+$, 11), 240 (100), 211 (24), 196 (42), 165 (24), 153 (25); FTIR (KBr, cm^{-1}) 2934, 1633, 1455, 1379, 1288, 1223, 1109, 1035; HRMS (EI-TOF) m/z [M − H]$^+$ for $C_{20}H_{24}NO_2$: calcd, 310.1807; found, 310.1792.

***N,N*-Diethyl-4-methoxy-3-trimethylsilyl-2′,3′-dimethylbiphenyl-2-carboxamide (3h).** Compound **1i** was synthesized according to general procedure A using TMEDA (3.1 mL, 20.7 mmol, 1.30 equiv), *s*-BuLi (1.23 M in cyclohexane, 16.8 mL, 20.7 mmol, 1.30 equiv) in THF (40 mL), **1k** (4.45 g, 15.9 mmol, 1.0 equiv) in THF (30 mL), and tri*iso*propylborate (11.0 mL, 47.8 mmol, 3.0 equiv). After standard workup (quench with sat. aq. NH_4Cl and ether extraction), crude **1i** (5.32 g, 103%) was isolated and used in the next step without further purification.

The title compound **3h** was synthesized according to general procedure E using **1i** (5.32 g, 15.9 mmol, 1.4 equiv), **2b** (2.09 g, 11.3 mmol, 1.00 equiv), 2 M aqueous Na_2CO_3 (40 mL), and Pd(PPh_3)$_4$ (394 mg, 0.34 mmol, 3.0 mol %) in 80 mL of dimethoxyethane. After standard workup, the residue was purified via column chromatography using heptane/ethyl acetate (6:1) to afford the title product as a colorless oil that solidifies (3.59 g, 83% yield). mp 95−96 °C (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two rotamers: major (A) and minor (B)) δ 7.08−7.15 (B, m, 1H), 7.03 (A, d, J = 8.5 Hz, 1H), 6.98 (B, d, J = 8.3 Hz, 1H), 6.93 (A + B, d, J = 7.2 Hz, 2H), 6.89 (B, d, J = 7.5 Hz, 1H), 6.84 (A, t, J = 7.8 Hz, 1H), 6.75 (A, d, J = 7.5 Hz, 1H), 6.72 (A, d, J = 4.2 Hz, 1H), 6.70 (B, d, J = 4.3 Hz, 1H), 3.71 (A, s, 3H), 3.70 (B, s, 3H), 3.50−3.65 (A + B, m, 2H), 3.02 (B, sex, J = 7.0 Hz, 1H), 2.91 (A, sex, J = 7.0 Hz, 1H), 2.65 (B, sex, J = 7.1 Hz, 1H), 2.54 (A, sex, J = 7.0 Hz, 1H), 2.46 (A, sex, J = 6.5 Hz, 1H), 2.35 (B, sex, J = 6.5 Hz, 1H), 2.15 (A, s, 3H), 2.11 (B, s, 3H), 1.96 (A, s, 3H), 1.86 (B, s, 3H), 0.83 (B, t, J = 7.2 Hz, 3H), 0.68 (A, t, J = 7.2 Hz, 3H), 0.40 (A, t, J = 7.1 Hz, 3H), 0.22 (B, t, J = 7.1 Hz, 3H), 0.14 (B, s, 9H), 0.13 (A, s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.6, 0.7, 10.7, 11.4, 12.8, 12.9, 17.1, 17.7, 20.4, 20.7, 37.0, 37.6, 42.4, 42.5, 55.1, 55.2, 109.0, 109.2, 123.8, 123.9, 124.8, 124.8, 127.1, 128.6, 128.7, 129.5, 130.2, 131.7, 132.0, 133.3, 133.6, 136.5, 136.7, 137.2, 138.8, 140.0, 142.8, 143.3, 163.8, 163.9, 169.2, 169.5; MS (EI, DIP) m/z 383 (M$^+$, 6), 368 (100), 311 (9), 295 (7); FTIR (KBr, cm^{-1}) 2980, 2933, 1633, 1429, 1282, 1239, 1061; HRMS (EI-TOF) m/z [M]$^+$ for $C_{23}H_{33}NO_2Si$: calcd, 383.2281; found, 383.2293.

***N,N*-Diethyl-4-methoxy-3-trimethylsilyl-2′-methylbiphenyl-2-carboxamide (3i).** The title compound was synthesized according to general procedure C using **1l** (550 mg, 1.36 mmol, 1.0 equiv), **2c** (370 mg, 2.72 mmol, 2.0 equiv), 2 M aqueous K_2CO_3 (4 mL, 8.00 mmol, 5.9 equiv), and Pd(dppf)Cl_2·CH_2Cl_2 (54 mg, 0.066 mmol, 4.9 mol %) in 14 mL of dioxane. After standard workup, the residue was purified via column chromatography using hexanes/EtOAc (9:1 to 5:1 gradient) to afford the title product as a colorless oil that solidifies (475 mg, 95% yield). mp 74−77 °C (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two rotamers: major (A) and minor (B)) δ 7.41 (A, d, J = 7.4 Hz, 1H), 7.00−7.28 (A + B, m, 9H), 6.86 (A, d, J = 4.7 Hz, 1H), 6.84 (B, d, J = 5.2 Hz, 1H), 3.84 (B, s, 3H), 3.84 (A, s, 3H), 3.66−3.80 (A + B, m, 2H), 3.20 (B, sex, J = 7.0 Hz, 1H), 3.06 (A, sex, J = 7.0 Hz, 1H), 2.85 (B, sex, J = 7.0 Hz, 1H), 2.71 (A, sex, J = 7.0 Hz, 1H), 2.60 (A, sex, J = 6.7 Hz, 1H), 2.51 (B, sex, J = 6.7 Hz, 1H), 2.22 (A, s, 3H), 2.15 (B, s, 3H), 0.99 (B, t, J = 7.1 Hz, 3H), 0.84 (A, t, J = 7.1 Hz, 3H), 0.55 (A, t, J = 7.1 Hz, 3H), 0.39 (B, t, J = 7.0 Hz, 3H), 0.29 (A, s, 9H), 0.28 (B, s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.6, 0.6, 10.8, 11.4, 12.8, 20.3, 20.4, 36.9, 37.4, 42.2, 42.3, 55.0, 55.1, 108.9, 109.1, 123.9, 124.1, 124.7, 125.2, 127.0, 127.3, 129.0, 129.5, 129.5, 129.8, 131.3, 131.5, 131.6, 132.9, 135.0, 138.6, 138.7, 140.0, 142.8, 143.3, 163.8, 169.1, 169.3; MS (EI, DIP) m/z 369 (M$^+$, 17), 354 (92), 297 (15), 264 (27), 219 (100), 131 (33), 108 (32); FTIR (KBr, cm^{-1}) 2975, 1633, 1452, 1425, 1284, 1242, 1059; HRMS (EI-TOF) m/z [M]$^+$ for $C_{22}H_{31}NO_2Si$: calcd, 369.2124; found, 369.2125.

***N,N*-Diethyl-6-methoxy-2′-methyl-5′-fluorobiphenyl-2-carboxamide (3j).** The title compound was synthesized according to general procedure D using **1f** (166 mg, 0.5 mmol, 1.0 equiv), **2f** (115 mg, 0.75 mmol, 1.5 equiv), K_3PO_4 (530 mg, 2.5 mmol, 5.0 equiv), Pd_2dba_3 (10 mg, 0.011 mmol, 2.2 mol %), and SPhos (16 mg, 0.039 mmol, 7.8 mol %) in 4 mL of toluene. After standard workup, the residue was purified via column chromatography using pentane/Et_2O (2:1 to 1:1 gradient) to afford the title product as a pale yellow solid (119 mg, 75% yield). mp 113−114 °C (cyclohexane); ^{1}H NMR (400 MHz, DMSO-d_6, 70 °C) δ 7.42 (t, J = 7.6 Hz, 1H), 7.20 (dd, J = 6.2, 8.3 Hz, 1H), 7.13 (dd, J = 0.6, 8.3 Hz, 1H), 6.99 (dt, J = 2.8, 8.6 Hz, 1H), 6.89 (dd, J = 0.9, 7.6 Hz, 1H), 6.82 (dd, J = 2.4, 9.8 Hz, 1H), 3.73 (s, 3H), 2.80−3.40 (br m, 4H), 2.00 (s, 3H), 0.94 (br s, 3H), 0.65 (t, J = 6.8 Hz, 3H); despite measurement of dilute and concentrated samples and varying the number of scans, NMR solvents, and temperature, a ^{13}C NMR showing adequate signal intensities could not be obtained; MS (EI, DIP) m/z 315 (M$^+$, 87), 242 (100), 183 (9), 74 (29); FTIR (KBr, cm^{-1}) 2973, 2934, 1632, 1574, 1462, 1427, 1297, 1256, 1059, 891, 801; HRMS (ESI-TOF) m/z [M + H]$^+$ for $C_{19}H_{23}FNO_2$: calcd, 316.1713; found, 316.1712.

***N,N*-Diethyl-4-methoxy-2′,3′-dimethylbiphenyl-2-carboxamide (3k).** The title compound was synthesized according to general procedure F with **3h** (3.37 g, 8.79 mmol, 1.0 equiv) and TBAF (1 M in THF, 21.6 mL, 2.46 equiv) in THF (18 mL). After standard workup, the residue was purified via column chromatography using heptane/ethyl acetate (1:1) to afford the title compound as a colorless solid (2.56 g, 94%). mp 102−103 °C (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85−7.24 (m, 6H), 3.85 (s, 3H), 3.72 (br s, 1H), 2.50−3.20 (m, 3H), 2.28 (s, 3H), 2.08 (br s, 3H), 0.50−1.05 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7, 13.7, 17.1, 20.6, 37.9, 42.4, 55.4, 114.2, 128.9, 136.8, 158.6, 169.9; MS (EI, DIP) m/z 311 (M$^+$, 5), 282 (1), 239 (55), 238 (100), 224 (10), 211 (13), 196 (14), 181 (11), 165 (11), 152 (13); FTIR (KBr, cm^{-1}): 3059, 2971, 2929, 1627, 1479, 1461, 1292, 1230, 1077, 1042; HRMS (EI-TOF) m/z [M − H]$^+$ for $C_{20}H_{24}NO_2$: calcd, 310.1807; found, 310.1800.

***N,N*-Diethyl-4-methoxy-2′-methylbiphenyl-2-carboxamide (3l).** The title compound was synthesized according to general procedure F with **3i** (1.19 g, 3.21 mmol, 1.0 equiv) and TBAF (1 M in THF, 3.5 mL, 1.1 equiv) in THF (30 mL). After standard workup, the residue was purified via column chromatography using hex/EtOAc (7:1 to 1:1 gradient) to afford the title compound as a colorless oil (796 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07−7.24 (m, 5H), 6.94 (dd, J = 2.6, 8.4 Hz, 1H), 6.90 (s, 1H), 3.85 (s, 3H), 3.73 (br s, 1H), 2.50−3.35 (m, 3H), 2.21 (s, 3H), 0.89 (br s, 3H), 0.68 (t, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7, 13.7, 20.2, 37.8,

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42.2, 55.4, 111.3, 114.2, 125.2, 127.0, 130.0, 131.4, 138.1, 158.7, 169.8; MS (EI, DIP) m/z 297 (M^+, 4), 224 (100), 197 (44), 182 (38), 165 (29), 153 (33); FTIR (KBr, cm^{-1}) 3058, 2971, 2933, 2836, 1635, 1566, 1456, 1379, 1289, 1229, 1082, 1002, 831; HRMS (EI-TOF) m/z $[M]^+$ for $C_{19}H_{23}NO_2$: calcd, 297.1729; found, 297.1720.

***N,N*-Diethyl-3-methyl-2′-methylbiphenyl-2-carboxamide (4a).** The title compound was synthesized according to general procedure A by dissolving **3a** (1.73 g, 6.47 mmol, 1.0 equiv) in THF (60 mL) and adding TMEDA (1.16 mL, 7.76 mmol, 1.2 equiv) and *s*-BuLi (1.16 M in cyclohexane, 6.69 mL, 7.76 mmol, 1.2 equiv) at −78 °C. After 1 h, MeI (2.00 mL, 35.3 mmol, 5.0 equiv) in THF (5 mL) was precooled to −78 °C and added all at once. After standard workup, the residue was purified via column chromatography using heptane/ethyl acetate (2:1). The title compound was isolated as a colorless oil (1.73 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$, two rotamers: ∼1:1 ratio) δ 7.35−7.50 (m, 2H), 6.94−7.34 (m, 12H), 3.56−3.76 (m, 2H), 3.13−3.30 (m, 1H), 2.78−3.11 (m, 4H), 2.60−2.77 (m, 1H), 2.35 (s, 6H), 2.23 (s, 3H), 2.16 (s, 3H), 1.00 (br s, 3H), 0.82 (br s, 3H), 0.70 (br s, 3H), 0.60 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.4, 11.7, 13.5, 13.6, 19.4, 19.5, 20.2, 37.1, 37.5, 41.8, 42.2, 124.3, 125.4, 126.9, 127.3, 127.5, 128.0, 128.4, 129.1, 129.8, 130.0, 131.1, 133.8, 134.8, 136.4, 136.6, 137.2, 137.8, 138.7, 138.8, 140.1, 169.3, 169.4; MS (EI, DIP) m/z 281 (M^+, 14), 266 (34), 209 (100), 165 (66); FTIR (KBr, cm^{-1}) 2972, 2931, 1630, 1492, 1283; HRMS (EI-TOF) m/z $[M]^+$ for $C_{19}H_{23}NO$: calcd, 281.1780; found, 281.1772.

***N,N*-Diethyl-3-chloro-2′-methylbiphenyl-2-carboxamide (4b).** The title compound was synthesized according to general procedure A using TMEDA (120 μL, 0.80 mmol, 2.1 equiv), *s*-BuLi (1.1 M in cyclohexane, 730 μL, 0.80 mmol, 2.1 equiv) in THF (1.0 mL), **3a** (100 mg, 0.37 mmol, 1.0 equiv) in THF (1.0 mL), and C_2Cl_6 (266 mg, 1.12 mmol, 3.0 equiv), in THF (0.5 mL). After standard workup, the residue was purified via column chromatography using CH_2Cl_2/Et_2O (10:0 to 10:1 gradient). The title compound was isolated as a colorless solid (79 mg, 70%). mp 87 °C (cyclohexane); ^{1}H NMR (400 MHz, DMSO-d_6, 70 °C) δ 7.39−7.55 (m, 2H), 7.08−7.32 (m, 5H), 3.44 (sext, J = 6.6 Hz, 1H), 2.75−3.33 (m, 3H), 2.12 (s, 3H), 0.96 (br s, 3H), 0.64 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6, 70 °C) δ 11.9, 13.8, 20.3, 37.6, 42.4, 125.4, 128.4, 128.7, 129.4, 129.8, 130.3, 136.5, 165.7; MS (EI, DIP) m/z 301 (M^+, 3), 264 (41), 229 (32), 219 (100), 165 (48), 131 (79), 114 (14), 100 (25), 69 (99); FTIR (KBr, cm^{-1}) 2977, 2929, 2870, 1634, 1464, 1283; HRMS (EI-TOF) m/z $[M]^+$ for $C_{18}H_{20}ClNO$: calcd, 301.1233; found, 301.1253.

***N,N*-Diethyl-3-trimethylsilyl-2′-methylbiphenyl-2-carboxamide (4c).** The title compound was synthesized according to general procedure A using TMEDA (120 μL, 0.80 mmol, 2.1 equiv), *s*-BuLi (1.1 M in cyclohexane, 730 μL, 0.80 mmol, 2.1 equiv) in THF (1.0 mL), **3a** (100 mg, 0.37 mmol, 1.0 equiv) in THF (1.0 mL), and TMSCl (140 μL, 1.12 mmol, 3.0 equiv). After standard workup, the residue was purified via column chromatography using CH_2Cl_2/Et_2O (100:0 to 95:5 gradient). The title compound was isolated as a colorless oil (116 mg, 92%). ^{1}H NMR (400 MHz, DMSO-d_6, 70 °C) δ 7.60 (d, J = 7.4 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.08−7.36 (m, 4H), 3.56 (sex, J = 6.6 Hz, 1H), 2.96 (br s, 1H), 2.71 (br s, 2H), 2.18 (br s, 3H), 0.76 (br s, 3H), 0.57 (br s, 3H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6, 2 rotamers) δ −0.1, 0.0, 10.9, 11.5, 12.6, 12.6, 19.8, 20.0, 36.2, 37.0, 41.9 (2 × C), 124.5, 125.0, 126.6, 126.7, 127.3 (2 × C), 127.5, 127.5, 128.9, 129.1, 129.8, 129.8, 130.2, 130.3, 130.9, 133.5, 133.7, 134.7, 135.9, 137.,4 138.3, 138.3, 141.7 (2 × C), 169.2 (2 × C); MS (EI, DIP) m/z 339 (M^+, 26), 324 (100), 267 (70), 264 (29), 251 (48), 235 (14), 219 (74), 195 (17), 178 (19), 165 (33), 131 (52), 73 (34), 69 (72); FTIR (neat, cm^{-1}) 2962, 1626, 1439, 1281, 1246; HRMS (EI-TOF) m/z $[M]^+$ for $C_{21}H_{29}NOSi$: calcd, 339.2018; found, 339.2027.

***N,N*-Diethyl-6-methoxy-3-methyl-2′-methylbiphenyl-2-carboxamide (4d).** According to general procedure A, TMEDA (2.2 equiv, 3.33 mmol, 500 μL), *s*-BuLi (2.2 equiv, 3.33 mmol, 3.1 mL, 1.05 M in cyclohexane) in 5 mL of THF, and **3e** (1.0 equiv, 1.51 mmol, 450 mg) in THF (3 mL) were used. After a deprotonation time of 1 h, MeI (3.0 equiv, 4.50 mmol, 282 μL) was added all at once. Subsequent standard workup and flash column chromatography (CH_2Cl_2/Et_2O, 12:1) gave 366 mg (78%) of **4d** as a pale yellow oil that solidifies over time. It is possible to separate the rotamers via column chromatography, but the purified material converts back to a mixture over time. ^{1}H NMR (400 MHz, $CDCl_3$, rotamer A) δ 7.06−7.25 (m, 4H), 7.00 (d, J = 8.4 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 3.69 (s, 3H), 3.58−3.72 (m, 1H), 3.30 (sex, J = 7.0 Hz, 1H), 2.97 (sex, J = 7.0 Hz, 1H), 2.85 (sex, J = 6.7 Hz, 1H), 2.27 (s, 3H), 2.13 (s, 3H), 1.05 (t, J = 7.1 Hz, 3H), 0.60 (t, J = 7.1 Hz, 3H); ^{1}H NMR (400 MHz, $CDCl_3$, rotamer B) δ 7.30−7.40 (m, 1H), 7.12−7.24 (m, 4H), 6.84 (d, J = 8.4 Hz, 1H), 3.70 (s, 3H), 3.62 (sex, J = 6.6 Hz, 1H), 3.06 (sex, J = 7.0 Hz, 1H), 2.86 (sex, J = 6.6 Hz, 1H), 2.67 (sex, J = 7.0 Hz, 1H), 2.27 (s, 3H), 2.12 (s, 3H), 0.85 (t, J = 7.1 Hz, 3H), 0.61 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rotamer A) δ 11.4, 13.6, 18.5, 20.1, 36.9, 42.2, 55.7, 110.6, 124.3, 125.4, 127.1, 127.5, 128.6, 129.7, 130.1, 135.8, 137.9, 138.3, 154.8, 168.7; ^{13}C NMR (100 MHz, $CDCl_3$, rotamer B) δ 11.5, 13.5, 18.6, 19.4, 37.0, 41.6, 55.5, 110.3, 125.3, 126.0, 126.2, 127.3, 128.9, 130.2, 131.3, 134.8, 136.6, 138.3, 154.7, 168.8; MS (ESI) m/z 312 (M^+ + H, 100); FTIR (KBr, cm^{-1}) 2967, 2935, 1620, 1473, 1460, 1291, 1251, 1060, 759; HRMS (ESI-TOF) m/z $[M + H]^+$ for $C_{20}H_{26}NO_2$: calcd, 312.1958; found, 312.1956.

***N,N*-Diethyl-5-methoxy-3-methyl-2′-methylbiphenyl-2-carboxamide (4e).** According to general procedure A, TMEDA (2.2 equiv, 3.33 mmol, 500 μL), *s*-BuLi (2.2 equiv, 3.33 mmol, 3.4 mL, 0.97 M in cyclohexane) in 8 mL of THF, and **3f** (1.0 equiv, 1.51 mmol, 450 mg) in THF (3 mL) were used. After a deprotonation time of 1 h, MeI (3.0 equiv, 4.50 mmol, 282 μL) was added all at once. Subsequent standard workup and flash column chromatography (hexanes/EtOAc, 2:1) gave the title compound as a colorless oil (360 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two rotamers: ∼1:1 ratio) δ 7.34−7.45 (m, 1H), 7.00−7.25 (m, 7H), 6.75 (d, J = 2.1 Hz, 2H), 6.64 (s, 1H), 6.55 (s, 1H), 3.80 (s, 6H), 3.63 (br s, 2H), 3.21 (br s, 1H), 3.05 (br s, 1H), 2.92 (br s, 1H), 2.84 (br s, 2H), 2.69 (br s, 1H), 2.32 (s, 6H), 2.26 (s, 3H), 2.18 (s, 3H), 0.98 (br s, 3H), 0.81 (br s, 3H), 0.68 (br s, 3H), 0.58 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.5, 11.7, 13.6, 13.7, 19.7, 19.7, 20.3 (2C), 37.2, 37.4, 41.9, 42.3, 55.2 (2C), 112.2, 113.2, 114.6, 114.7, 124.3, 125.4, 127.5 (2C), 128.2, 129.8, 130.0, 131.0, 134.6, 134.6, 135.6, 135.6, 136.5, 137.7, 137.7, 138.7, 158.2, 158.3, 158.8, 158.9, 169.4 (2C); MS (EI, DIP) m/z 311 (M^+, 4), 296 (12), 239 (100), 196 (16), 165 (17); FTIR (KBr, cm^{-1}) 2971, 2837, 1632, 1462, 1380, 1327, 1284, 1206, 1164, 1050, 857 HRMS (EI-TOF) m/z $[M]^+$ for $C_{20}H_{25}NO_2$: calcd, 311.1885; found, 311.1881.

***N,N*-Diethyl-4-methoxy-3-methyl-2′-methylbiphenyl-2-carboxamide (4f).** According to general procedure A, TMEDA (2.2 equiv, 2.40 mmol, 360 μL), *s*-BuLi (2.2 equiv, 2.40 mmol, 2.0 mL, 1.20 M in cyclohexane) in 10 mL of THF, and **3l** (1.0 equiv, 1.09 mmol, 325 mg) in THF (10 mL) were used. After a deprotonation time of 1 h, MeI (3.0 equiv, 3.28 mmol, 205 μL) was added all at once. Subsequent standard workup and flash column chromatography (CH_2Cl_2/Et_2O, 12:1) gave **4f** as a pale yellow oil that solidifies (303 mg, 89%). mp 114−115 °C (cyclohexane); ^{1}H NMR (400 MHz, DMSO-d_6, 70 °C) δ 7.06−7.23 (m, 4H), 6.95−7.05 (m, 2H), 3.86 (s, 3H), 3.45 (sex, J = 6.6 Hz, 1H), 3.05 (sex, J = 6.5 Hz, 1H), 2.91 (sex, J = 6.6 Hz, 1H), 2.77 (sex, J = 6.5 Hz, 1H), 2.12 (br s, 3H), 2.09 (s, 3H), 0.85 (br s, 3H), 0.62 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 70 °C) δ 12.1, 13.3, 13.8, 20.5, 37.4, 42.2, 56.2, 110.5, 122.4, 125.2, 127.6, 128.8, 130.1, 130.4, 136.7, 138.5, 139.8, 157.1, 168.5; MS (EI, DIP) m/z 311 (M^+, 20), 297 (24), 263 (19), 239 (48), 219 (100, 131 (29); FTIR (KBr, cm^{-1}) 2973, 2836, 1631, 1468, 1379, 1286, 1222, 1139, 1087; HRMS (EI-TOF) m/z $[M]^+$ for $C_{20}H_{25}NO_2$: calcd, 311.1885; found, 311.1884.

***N,N*,3-Triethyl-5-methoxy-2′-methylbiphenyl-2-carboxamide (4g).** According to general procedure A, a solution of **3f** (1.0 equiv, 4.02 mmol, 1.19 g) in THF (10 mL) was slowly added to a mixture of TMEDA (1.2 equiv, 4.82 mmol, 0.72 mL) and *s*-BuLi (1.2 equiv, 4.82 mmol, 3.92 mL) in THF (10 mL) while the temperature was kept below −74 °C. After 1 h of deprotonation time, MeI (4.8 equiv, 19.3 mmol, 1.20 mL) was slowly added. After approximately 0.4 mL of MeI was added, due to a fire alarm, the reaction mixture was left at −78 °C for 30 min before addition of MeI to the now blood red mixture was continued. After standard workup the product was

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fractionated by flash chromatography (heptane/EtOAc, 2:1) into **4g** (254 mg, colorless oil), a mixture of **4g** and **4e** (377 mg), and a mixture of **4e** and **3f** (346 mg). From integrations of the relative ^{1}H NMR spectra, this corresponded to 34% **4g**, 24% **4e**, and 20% starting material (**3f**): ^{1}H NMR (400 MHz, $CDCl_3$, mixture of two rotamers: ~1:1 ratio) δ 7.41 (d, J = 6.9 Hz, 1H), 7.02−7.24 (m, 7H), 6.76−6.86 (m, 2H), 6.64 (s, 1H), 6.54 (s, 1H), 3.79 (s, 6H), 3.52−3.72 (m, 1H), 3.12−3.26 (m, 1H), 2.98−3.12 (m, 1H), 2.86−2.98 (m, 1H), 2.76−2.86 (m, 2H), 2.50−2.76 (m, 5H), 2.26 (s, 3H), 2.17 (s, 3H), 1.27 (t, J = 7.6 Hz, 6H), 0.94 (t, J = 6.4 Hz, 3H). 0.78 (t, J = 6.6 Hz, 3H), 0.66 (t, J = 6.7 Hz, 3H), 0.53 (t, J = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.2, 11.5, 13.4, 13.6, 14.8, 14.9, 20.2 (2C), 26.0, 26.3, 37.0, 37.3, 41.9, 42.2, 55.1 (2C), 111.8, 112.6, 113.0 (2C), 124.2, 125.3, 127.4 (2C), 128.2, 128.7, 129.1, 129.7, 130.0, 130.9, 134.6, 137.6, 138.4, 138.7, 140.0, 141.7, 142.7, 158.4, 159.0, 169.1, 169.3; MS (EI, DIP) m/z 325 (M^+, 6), 296 (16), 253 (100); FTIR (KBr, cm^{-1}) 2968, 2934, 1627, 1597, 1456, 1423, 1285, 1205, 1163, 1035; HRMS (EI-TOF) m/z $[M]^+$ for $C_{21}H_{27}NO_2$: calcd, 325.2042; found, 325.2031.

8-Methylphenanthren-9-ol (5b). The title compound was synthesized according general procedure B from prepared LDA (DIPA, 2.37 mL, 16.9 mmol, 2.75 equiv; n-BuLi, 2.04 M, 7.52 mL, 15.3 mmol, 2.5 equiv) in THF (50 mL) and **4a** (1.73g, 6.14 mmol, 1.0 equiv) in THF (15 mL). The reaction was stirred at 0 °C for 1.5 h, and after a standard workup, the residual solids was purified by flash chromatography using heptane/ethyl acetate (4:1 to 3:1 gradient) to give **5b** as a tan solid (1.1343 g, 89%) that darkened rapidly when wet. Due to rapid decomposition, no clean ^{1}H NMR or melting point could be obtained. Additionally, the MS indicated the oxidized 9,10-phenanthraquinone as the major component as described below. ^{1}H NMR (400 MHz, acetone-d_6) δ 9.11 (br s, 1H), 8.69 (d, J = 6.4 Hz, 1H), 8.67 (d, J = 6.4 Hz, 1H), 7.69 (dd, J = 1.4, 7.9 Hz, 1H), 7.41−7.59 (m, 4H), 7.15 (s, 1H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 24.7, 106.4, 121.0, 123.0, 123.5, 125.9, 126.6, 126.8, 129.9, 133.1, 136.0, 153.8; MS (EI, DIP) oxidized diquinone m/z 245 ($[M + Na]^+$, 100), 223 (8); FTIR (KBr, cm^{-1}) 3412, 1671, 1591, 1454, 1224, 760; HRMS (ESI-TOF) m/z $[M + H]^+$ for $C_{15}H_{13}O$: calcd, 209.0961; found, 209.0958.

***N,N*-Diethyl-1-methylphenanthren-9-yl Diethylcarbamate (6a).** The title compound was synthesized according general procedure B from prepared LDA (DIPA, 2.08 mL, 14.8 mmol, 2.75 equiv; n-BuLi, 2.04 M, 6.62 mL, 13.5 mmol, 2.5 equiv) in THF (45 mL) and **3b** (1.52 g, 5.40 mmol, 1.0 equiv) in THF (15 mL). The reaction was stirred at 0 °C for 1 h, followed by a standard workup to yield 1.17 g of residue. The residue (1.15 g) was subjected directly to a carbamoylation reaction by dissolving the residue in THF (25 mL), and after cooling to 0 °C, NaH (60%, 0.331g, 8.28 mmol, 1.5 equiv) was added. After stirring for 15 min, diethylcarbamoyl chloride (1.40 mL, 11.0 mmol, 2.0 equiv) was added in one portion, and the reaction mixture was stirred overnight at room temperature. After quenching with sat. aq. NH_4Cl (30 mL) and diethyl ether extraction (3 × 30 mL), the dried ($MgSO_4$) and evaporated residue was subjected to column chromatography using heptane/ethyl acetate (4:1 to 2.5:1, gradient) as eluent. The title compound was obtained as a colorless solid (1.36 g, 82%). mp 99−100 °C (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 8.1 Hz, 1H), 8.55 (d, J = 8.3 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.76 (s, 1H), 7.59−7.61 (m, 2H), 7.52 (t, J = 7.9 Hz, 1H), 7.44 (d, J = 7.0 Hz, 1H), 3.68 (q, J = 7.0 Hz, 2H), 3.50 (q, J = 7.0 Hz, 2H), 2.74 (s, 3H), 1.44 (t, J = 6.9 Hz, 3H), 1.29 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 14.5, 20.0, 42.0, 42.3, 114.1, 120.7, 121.9, 123.2, 125.7, 126.6, 126.9, 127.0, 128.0, 128.8, 130.8, 131.9, 134.6, 145.6, 154.3; MS (EI, DIP) m/z 307 (M^+, 59), 189 (8), 179 (51), 178 (58), 100 (100); FTIR (KBr, cm^{-1}) 1717; HRMS (EI-TOF) m/z $[M]^+$ for $C_{20}H_{21}NO_2$: calcd, 307.1572; found, 307.1562.

7-Methoxy-8-methylphenanthren-9-yl Trifluoromethanesulfonate (6b). The title compound was synthesized according general procedure B from prepared LDA (DIPA, 694 μL, 4.95 mmol, 2.75 equiv; n-BuLi, 1.1 M, 4.09 mL, 4.5 mmol, 2.5 equiv) in THF (20 mL) and **4f** (560 mg, 1.80 mmol, 1.0 equiv) in THF (7 mL). The reaction was stirred at −20 °C for 15 min and then at room temperature for another hour. After a standard workup, the residual colorless solid was directly used for next step without further purification. The residue was dissolved in CH_2Cl_2 (30 mL) and cooled to 0 °C. The solution was treated with pyridine (218 μL, 2.70 mmol, 1.50 equiv) and triflic anhydride (454 μL, 2.70 mmol, 1.50 equiv). The solution was warmed to room temperature overnight, water was added (40 mL), and the mixture was extracted with CH_2Cl_2 (2 × 25 mL). The organic phases were combined, dried ($MgSO_4$), and evaporated to dryness. The residue was purified via column chromatography using heptane/ethyl acetate (5:1) as eluent to afford the desired product as an amorphous brown solid (363 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (t, J = 9.6 Hz, 1H), 7.82 (dd, J = 7.8, 1.3 Hz, 1H), 7.72 (s, 1H), 7.60−7.70 (m, 1H), 7.50−7.60 (m, 1H), 7.39 (d, J = 9.2 Hz, 1H), 3.99 (s, 3H), 2.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 56.3, 113.0, 116.5, 120.0, 120.7, 122.1, 122.4, 126.0, 126.6, 127.1, 127.9, 128.5, 129.0, 130.3, 144.6, 157.1; MS (EI, DIP) m/z 370 (M^+, 10), 237 (100); FTIR (KBr, cm^{-1}) 2955, 2845, 1595, 1421, 1279, 1213, 1164, 1026, 818; HRMS (EI-TOF) m/z $[M]^+$ for $C_{17}H_{13}F_3O_4S_1$: calcd, 370.0486; found, 370.0465.

***N,N*-Diethyl-6-methoxy-8-methylphenanthren-9-yl Diethylcarbamate (6c).** The title compound was synthesized according general procedure B from prepared LDA (DIPA, 240 μL, 1.72 mmol, 2.2 equiv; n-BuLi, 2.15 M, 800 μL, 1.72 mmol, 2.2 equiv) in THF (22 mL) and **4e** (243 mg, 0.78 mmol, 1.0 equiv) in THF (5 mL). The reaction was stirred at 0 °C for 1 h, and after a standard workup, the residue was subjected directly to a carbamoylation reaction by dissolving the residue in THF (10 mL), and after cooling to 0 °C, NaH (60%, 47 mg, 1.17 mmol, 1.5 equiv) was added. After stirring for 30 min, diethylcarbamoyl chloride (150 μL, 1.17 mmol, 1.5 equiv) was added in one portion, and the reaction mixture was stirred overnight at room temperature. After quenching with sat. NH_4Cl (aq) and CH_2Cl_2 extraction (2 × 20 mL), the dried ($MgSO_4$) and evaporated residue was subjected to column chromatography (CH_2Cl_2). The title compound was obtained as a brown solid (115 mg, 44%). mp 112−114 °C (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52−8.59 (m, 1H), 7.99 (d, J = 2.3 Hz, 1H), 7.75−7.81 (m, 1H), 7.51−7.60 (m, 2H), 7.26 (s, 1H), 7.05 (d, J = 1.7 Hz, 1H), 4.00 (s, 3H), 3.60 (q, J = 7.1 Hz, 2H), 3.47 (q, J = 7.1 Hz, 2H), 2.81 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 14.3, 23.7, 41.7, 42.0, 55.2, 102.5, 116.9, 120.4, 121.6, 123.0, 125.6, 126.8, 127.8, 128.8, 132.0, 134.6, 135.7, 147.2, 154.8, 157.8; MS (EI, DIP) m/z 337 (M^+, 71), 284 (10), 219 (35), 165 (12), 100 (100), 72 (22); FTIR (KBr, cm^{-1}) 2972, 2935, 1716, 1609, 1465, 1419, 1377, 1262, 1219, 1155, 1051; HRMS (EI-TOF) m/z $[M]^+$ for $C_{21}H_{23}NO_3$: calcd, 337.1678; found, 337.1677.

***N,N*-Diethyl-5-methoxy-8-methylphenanthren-9-yl Diethylcarbamate (6d).** The title compound was synthesized according general procedure B from prepared LDA (DIPA, 353 μL, 2.51 mmol, 2.2 equiv; n-BuLi, 2.27 M, 1.10 mL, 2.51 mmol, 2.2 equiv) in THF (30 mL) and **4d** (355 mg, 1.14 mmol, 1.0 equiv) in THF (7 mL). The reaction was stirred at 0 °C for 1 h, and after a standard workup, the residue was subjected directly to a carbamoylation reaction by dissolving the residue in THF (15 mL), and after cooling to 0 °C, NaH (60%, 55 mg, 1.37 mmol, 1.2 equiv) was added. After stirring for 15 min, diethylcarbamoyl chloride (174 μL, 1.37 mmol, 1.2 equiv) was added in one portion, and the reaction mixture was stirred overnight at room temperature. After quenching with sat. NH_4Cl (aq) and CH_2Cl_2 extraction (3 × 20 mL), the dried ($MgSO_4$) and evaporated residue was subjected to column chromatography (CH_2Cl_2 to CH_2Cl_2 + 5% Et_2O gradient). The title compound was obtained as a brown oil (200 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (d, J = 8.4 Hz, 1H), 7.81 (dd, J = 1.8, 7.1 Hz, 1H), 7.50−7.64 (m, 2H), 7.42 (s, 1H), 7.33 (d, J = 8.1 Hz, 1H), 7.07 (d, J = 8.2 Hz, 1H), 4.07 (s, 3H), 3.60 (q, J = 7.1 Hz, 2H), 3.48 (q, J = 7.1 Hz, 2H), 2.80 (s, 3H), 1.36 (t, J = 7.0 Hz, 3H), 1.27 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 14.3, 23.6, 41.6, 42.0, 55.8, 108.8, 120.5, 123.5, 125.4, 125.7, 126.0, 127.3, 128.7, 128.8, 129.1, 130.4, 131.8, 146.7, 154.7, 157.3; MS (EI, DIP) m/z 337 (M^+, 19), 264 (29), 219 (100), 166 (5), 131 (36), 100 (33); FTIR (KBr, cm^{-1}) 2971, 2873, 1713, 1632, 1453, 1384, 1267, 1157, 1072, 1049, 959; HRMS (EI-TOF) m/z $[M]^+$ for $C_{21}H_{23}NO_3$: calcd, 337.1678; found, 337.1670.

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***N,N*-Diethyl-5-methoxy-1-methylphenanthren-9-yl Diethylcarbamate (6e).** The title compound was synthesized according general procedure B from prepared LDA (DIPA, 900 μL, 6.40 mmol, 2.5 equiv; *n*-BuLi, 1.92 M, 3.32 mL, 6.40 mmol, 2.5 equiv) in THF (8 mL) and **3d** (800 mg, 2.57 mmol, 1.0 equiv) in THF (8 mL). The reaction was stirred at 0 °C for 1 h, and after a standard workup, the residue was subjected directly to a carbamoylation reaction by dissolving the residue in THF (4 mL), and after cooling to 0 °C, NaH (60%, 120 mg, 2.99 mmol, 1.2 equiv) was added. After stirring for 15 min, diethylcarbamoyl chloride (360 μL, 2.83 mmol, 1.1 equiv) was added in one portion, and the reaction mixture was stirred overnight at room temperature. After quenching with sat. NH_4Cl (aq) and CH_2Cl_2 extraction (3 × 20 mL), the dried ($MgSO_4$) and evaporated residue was subjected to column chromatography (CH_2Cl_2 to CH_2Cl_2 + 5% Et_2O gradient). The title compound was obtained as a colorless solid (1.08 g, 77%). mp 129−130 °C (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, J = 8.6 Hz, 1H), 7.80 (s, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.51 (dd, J = 7.1, 8.6 Hz, 1H), 7.44 (d, J = 7.0 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 4.12 (s, 3H), 3.67 (q, J = 7.0 Hz, 2H), 3.49 (q, J = 7.0 Hz, 2H), 2.75 (s, 3H), 1.43 (t, J = 6.9 Hz, 3H), 1.29 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 14.5, 20.5, 42.0, 42.3, 55.8, 109.0, 114.3, 115.0, 122.5, 125.4, 126.6, 126.7, 127.4, 128.9, 129.5, 130.9, 133.7, 145.2, 154.4, 158.9; MS (EI, DIP) m/z 337 (M^+, 48), 285 (13), 264 (20), 219 (100), 131 (26), 100 (62); FTIR (KBr, cm^{-1}) 2972, 2935, 1716, 1575, 1455, 1291, 1267, 1151, 1049, 1025, 746; HRMS (EI-TOF) m/z $[M]^+$ for $C_{21}H_{23}NO_3$: calcd, 337.1678; found, 337.1686.

5-Methoxy-1-methylphenanthren-9-yl Trifluoromethanesulfonate (6f). The title compound was synthesized according general procedure B from prepared LDA (DIPA, 316 μL, 2.4 mmol, 2.4 equiv; *n*-BuLi, 2.17 M, 1.03 mL, 2.2 mmol, 2.2 equiv) in THF (30 mL) and **3d** (311 mg, 1.0 mmol, 1.0 equiv) in THF (5 mL). The reaction was stirred at 0 °C overnight, and after a standard workup, the residual colorless solid was directly used for the next step without further purification. The residue was dissolved in CH_2Cl_2 (10 mL) and cooled to 0 °C. The solution was treated with pyridine (100 μL, 1.24 mmol, 1.24 equiv) and triflic anhydride (200 μL, 1.19 mmol, 1.19 equiv). The solution was warmed to room temperature overnight and evaporated to dryness. The residue was purified via column chromatography using pentane/DCM (7:1) as eluent to afford the desired product as a colorless solid (340 mg, 92%). The compound was converted without further purification to **7e**. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.55 (d, J = 8.7 Hz, 1H), 8.07 (s, 1H), 7.83 (t, J = 8.1 Hz, 1H), 7.63−7.72 (m, 2H), 7.60 (d, J = 7.0 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 4.15 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.6, 57.2, 111.9, 113.7, 116.3, 122.5, 127.3, 127.4, 128.7, 129.3, 129.7, 130.2, 135.8, 144.4, 159.4.

***N,N*-Diethyl-6-methoxy-1-methylphenanthren-9-yl Diethylcarbamate (6g).** The title compound was synthesized according general procedure B from prepared LDA (DIPA, 350 μL, 2.0 mmol, 2.5 equiv; *n*-BuLi, 1.92 M, 1.30 mL, 2.50 mmol, 2.5 equiv) in THF (4 mL) and **3d** (312 mg, 1.00 mmol, 1.0 equiv) in THF (4 mL). The reaction was stirred at 0 °C for 1 h, and after a standard workup, the residue was subjected directly to a carbamoylation reaction by dissolving the residue in THF (6 mL), and after cooling to 0 °C, NaH (60%, 60 mg, 1.5 mmol, 1.5 equiv) was added. After stirring for 15 min, diethylcarbamoyl chloride (190 μL, 1.5 mmol, 1.5 equiv) was added in one portion, and the reaction mixture was stirred overnight at room temperature. After quenching with sat. NH_4Cl (aq) and CH_2Cl_2 extraction (3 × 20 mL), the dried ($MgSO_4$) and evaporated residue was subjected to column chromatography (CH_2Cl_2 to CH_2Cl_2 + 5% Et_2O gradient). The title compound was obtained as a colorless solid (252 mg, 77%). mp 130−131.5 °C (cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 8.2 Hz, 1H), 8.07 (d, J = 2.2 Hz, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.62 (s, 1H), 7.48 (t, J = 7.3 Hz, 1H), 7.43 (d, J = 7.0 Hz, 1H), 7.27 (dd, J = 2.3, 9.0 Hz, 1H), 4.02 (s, 3H), 3.66 (q, J = 6.8 Hz, 2H), 3.49 (q, J = 6.9 Hz, 2H), 2.72 (s, 3H), 1.42 (t, J = 6.7 Hz, 3H), 1.29 (t, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 14.5, 20.0, 42.0, 42.3, 55.4, 104.5, 111.7, 116.9, 120.7, 121.7, 123.5, 125.2, 128.0, 128.2, 131.4, 133.5, 134.7, 145.7, 154.3, 158.7; MS (EI, DIP) m/z 337 (M^+, 33), 209 (41), 166 (42), 100 (100), 72 (42); FTIR (KBr, cm^{-1}) 2976, 1713, 1617, 1459, 1381, 1265, 1235, 1157; HRMS (EI-TOF) m/z $[M]^+$ for $C_{21}H_{23}NO_3$: calcd, 337.1678; found,: 337.1678.

***N,N*-Diethyl-7-methoxy-1-methylphenanthren-9-yl Diethylcarbamate (6h).** The title compound was synthesized according general procedure B from prepared LDA (DIPA, 3.00 mL, 21.5 mmol, 2.75 equiv; *n*-BuLi, 2.04 M, 9.57 mL, 19.5 mmol, 2.5 equiv) in THF (60 mL) and **3k** (2.43 g, 7.81 mmol, 1.0 equiv) in THF (15 mL). The reaction was stirred at −20 °C for 15 min and then at room temperature for another hour. After a standard workup, the colorless residue was subjected directly to a carbamoylation reaction by dissolving the residue in THF (40 mL), and after cooling to 0 °C, NaH (60%, 468 mg, 11.7 mmol, 1.5 equiv) was added. After stirring for 15 min, diethylcarbamoyl chloride (2.00 mL, 15.7 mmol, 2.0 equiv) was added in one portion, and the reaction mixture was stirred overnight at room temperature. After quenching with sat. aq. NH_4Cl (50 mL) and diethyl ether extraction (3 × 50 mL), the dried ($MgSO_4$) and evaporated residue was subjected to column chromatography using heptane/ethyl acetate (3:1) as eluent. The title compound was obtained as a colorless solid (2.42 g, 92%). mp 112.5−113.5 °C (hexanes/DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 9.1 Hz, 1H), 8.44 (d, J = 8.3 Hz, 1H), 7.78 (s, 1H), 7.49 (t, J = 8.3 Hz, 1H), 7.38 (d, J = 7.1 Hz, 1H), 7.35 (d, J = 2.6 Hz, 1H), 7.31 (dd, J = 9.1, 2.7 Hz, 1H), 3.95 (s, 3H), 3.67 (br s, 2H), 3.51 (br s, 2H), 2.73 (s, 3H), 1.44 (br s, 3H), 1.31 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 14.5, 19.9, 42.0, 42.3, 55.2, 102.3, 114.6, 117.2, 120.2, 125.0, 125.7, 126.3, 127.0, 128.3, 128.8, 129.6, 134.6, 145.0, 154.2, 158.3; MS (EI, DIP) m/z 337 (M^+, 58), 237 (8), 209 (29), 166 (42), 100 (100), 72 (36); FTIR (KBr, cm^{-1}) 2986, 1703, 1275, 1155, 865, 793; HRMS (EI-TOF) m/z $[M]^+$ for $C_{21}H_{23}NO_3$: calcd, 337.1678; found, 337.1664.

***N,N*-Diethyl-8-methoxy-1-methylphenanthren-9-yl Diethylcarbamate (6i).** The title compound was synthesized according general procedure B from prepared LDA (DIPA, 2.54 mL, 18.1 mmol, 2.75 equiv; *s*-BuLi, 1.16 M, 14.2 mL, 16.5 mmol, 2.5 equiv) in THF (55 mL) and **3c** (2.05 g, 6.58 mmol, 1.0 equiv) in THF (20 mL). The reaction was stirred at −20 °C for 15 min and then at room temperature for another hour. Standard workup yielded 1.60 g of residue. A part of the residue (0.98 g, 4.11 mmol, 1.0 equiv) was subjected directly to a carbamoylation reaction by dissolving the residue in THF (50 mL), and after cooling to 0 °C, NaH (60%, 0.23g, 5.76 mmol, 1.4 equiv) was added. After stirring for 15 min, diethylcarbamoyl chloride (0.83 mL, 6.55 mmol, 1.6 equiv) was added in one portion, and the reaction mixture was stirred overnight at room temperature. After quenching with sat. aq. NH_4Cl (50 mL) and diethyleter extraction (3 × 50 mL), the dried ($MgSO_4$) and evaporated residue was subjected to column chromatography using heptane/ethyl acetate (3:1 to 2:1, gradient) as eluent. The title compound was obtained as a colorless solid (1.13 g, 81%). mp 166−167 °C (hexanes/DCM); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 8.3 Hz, 1H), 8.34 (d, J = 8.4 Hz, 1H), 7.57 (s, 1H), 7.56 (t, J = 8.2 Hz, 1H), 7.49 (t, J = 8.2 Hz, 1H), 7.42 (d, J = 7.0 Hz, 1H), 7.02 (d, J = 7.0 Hz, 1H), 3.93 (s, 3H), 3.61 (br s, 2H), 3.48 (br s, 2H), 2.72 (s, 3H), 1.39 (br s, 3H), 1.28 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 14.1, 19.7, 41.7, 41.9, 55.7, 107.4, 115.5, 115.9, 118.2, 121.4, 125.6, 127.0, 128.0, 128.7, 131.0, 134.1, 134.3, 145.4, 155.2, 156.2; MS (EI, DIP) m/z 337 (M^+, 85), 179 (27), 178 (31), 165 (23), 100 (100); FTIR (KBr, cm^{-1}) 1713; HRMS (EI-TOF) m/z $[M]^+$ for $C_{21}H_{23}NO_3$: calcd, 337.1678; found, 337.1686.

2-Methoxy-1-methylphenanthrene (7b). The title compound was synthesized according to general procedure G using **6b** (358 mg, 0.967 mmol, 1.00 equiv), Et_3N (410 μL, 2.90 mmol, 3.0 equiv), HCO_2H (80 μL, 2.1 mmol, 2.2 equiv), $PdOAc_2$ (11.2 mg, 0.050 mmol, 5 mol %), and PPh_3 (26.3 mg, 0.100 mmol, 10 mol %) in DMF (15 mL). After standard workup, the residue was purified via column chromatography using heptane/ethyl acetate (10:1 to 5:1 gradient) to afford the title compound as a colorless solid (157 mg, 73%). Further recrystallization from heptane afforded colorless crystals (103 mg, 48%). mp 161.5−162.2 °C (heptane, lit. 160.5−161 °C [ethanol][59]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 8.2 Hz, 1H), 8.57 (d, J = 9.1 Hz, 1H),

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7.95 (d, J = 9.2 Hz, 1H), 7.87 (dd, J = 1.3, 7.8 Hz, 1H), 7.76 (d, J = 9.2 Hz, 1H), 7.60−7.70 (m, 1H), 7.50−7.60 (m, 1H), 7.34 (d, J = 9.1 Hz, 1H), 3.99 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.9, 56.3, 111.8, 120.8, 121.5, 122.3, 122.7, 124.6, 125.6, 126.6, 127.2, 128.4, 130.6, 130.8, 132.0, 155.5; MS (EI, DIP) m/z 245 ([M + Na]$^+$, 15), 217 (8), 157 (8), 125 (10); FTIR (KBr, cm^{-1}) 2941, 1607, 1467, 1271, 1208, 1097, 809, 743; HRMS (ESI-TOF) m/z [M + Na]$^+$ for $C_{16}H_{14}ONa$: calcd, 245.0942; found, 245.0941.

3-Methoxy-1-methylphenanthrene (7c). The title compound was synthesized according to general procedure H using **6c** (120 mg, 0.36 mmol, 1.0 equiv), Ni(acac)$_2$ (10 mg, 0.04 mmol, 10 mol %), and *i*-PrMgCl·LiCl (1.0 M in THF, 1.6 mL, 1.60 mmol, 4.5 equiv) in Et_2O (7 mL). After standard workup, the residue was purified via column chromatography using pentane/CH_2Cl_2 (8:1) to afford the title compound as a colorless solid (59 mg, 75%). The product is contaminated with approximately 20% of impurities that could not be removed via column chromatography or recrystallization. mp 70−71 °C (DCM/hexanes, lit. 90 °C [alcohol][60]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 8.1 Hz, 1H), 7.96 (d, J = 2.1 Hz, 1H), 7.89 (d, J = 8.9 Hz, 1H), 7.58−7.73 (m, 3H), 7.13 (br s, 1H), 4.02 (s, 3H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 55.3, 101.8, 118.0, 122.6, 122.9, 124.2, 126.0, 126.4, 128.5, 130.1, 131.8, 132.1, 136.7, 157.8; MS (EI, DIP) m/z 222 (M$^+$, 83), 219 (100), 207 (10), 179 (29), 131 (20); FTIR (KBr, cm^{-1}) 2957, 1611, 1463, 1263, 1209, 1054, 862, 811; HRMS (EI-TOF) m/z [M]$^+$ for $C_{16}H_{14}O$: calcd, 222.1045; found, 222.1047.

4-Methoxy-1-methylphenanthrene (7d). The title compound was synthesized according to general procedure H using **6d** (190 mg, 0.56 mmol, 1.0 equiv), Ni(acac)$_2$ (15 mg, 0.058 mmol, 10 mol %), and *i*-PrMgCl·LiCl (0.6 M in THF, 2.35 mL, 1.41 mmol, 2.5 equiv) in Et_2O (12 mL). After standard workup, the residue was purified via column chromatography using pentane/CH_2Cl_2 (10:1) to afford the title compound as a colorless solid (110 mg, 88%). The product is contaminated with approximately 24% of impurities that could not be removed via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (d, J = 8.6 Hz, 1H), 7.92−7.98 (m, 2H), 7.84 (d, J = 9.1 Hz, 1H), 7.61−7.73 (m, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 8.1 Hz, 1H), 4.13 (s, 3H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 55.7, 107.9, 123.0, 125.3, 125.8, 126.3, 126.7, 127.6, 127.8, 128.1, 128.8, 130.6, 132.4, 132.8, 157.4; MS (EI, DIP) m/z 222 (M$^+$, 99), 207 (55), 179 (43), 100 (23), 86 (68), 84 (100); FTIR (KBr, cm^{-1}) 2932, 1573, 1449, 1244, 1204, 1100, 821; HRMS (EI-TOF) m/z [M]$^+$ for $C_{16}H_{14}O$: calcd, 222.1045; found, 222.1051.

5-Methoxy-1-methylphenanthrene (7e). The title compound was synthesized according to general procedure G using **6f** (290 mg, 0.78 mmol, 1.0 equiv), Et_3N (330 μL, 2.35 mmol, 3.0 equiv), HCO_2H (60 μL, 1.59 mmol, 2.0 equiv), $PdOAc_2$ (3.5 mg, 0.016 mmol, 2 mol %), and PPh_3 (8.2 mg, 0.031 mmol, 4 mol %) in DMF (8 mL). After standard workup, the residue was purified via column chromatography using pentane/CH_2Cl_2 (1:0 to 20:1 gradient) to afford the title compound as a colorless solid (130 mg, 75%). mp 72−74 °C (Et_2O, lit. 76−77 °C [alcohol][61]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (d, J = 8.7 Hz, 1H), 8.03 (d, J = 9.1 Hz, 1H), 7.79 (d, J = 9.1 Hz, 1H), 7.53−7.63 (m, 3H), 7.50 (d, J = 7.1 Hz, 1H), 7.18 (dd, J = 2.7, 6.3 Hz, 1H), 4.15 (s, 3H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 55.7, 108.4, 121.2, 121.5, 123.5, 125.8, 126.4, 126.8, 126.9, 127.3, 130.4, 131.3, 133.9, 134.3, 158.8; MS (EI, DIP) m/z 222 (M$^+$, 81), 219 (100), 207 (28), 131 (25), 88 (37), 70 (43); FTIR (KBr, cm^{-1}) 3053, 2927, 1574, 1453, 1265, 1105, 1053, 824; HRMS (EI-TOF) m/z [M]$^+$ for $C_{16}H_{14}O$: calcd, 222.1045; found, 222.1041.

6-Methoxy-1-methylphenanthrene (7f). The title compound was synthesized according to general procedure H using **6g** (160 mg, 0.47 mmol, 1.0 equiv), Ni(acac)$_2$ (14 mg, 0.054 mmol, 11 mol %), and *i*-PrMgCl·LiCl (1.0 M in THF, 1.2 mL, 1.18 mmol, 2.5 equiv) in Et_2O (12 mL). After standard workup, the residue was purified via column chromatography using pentane/CH_2Cl_2 (6:1) to afford the title compound as a colorless solid (88 mg, 83%). The product is contaminated with approximately 16% of impurities that could not be removed via column chromatography or recrystallization. mp 77−80 °C (cyclohexane, lit. 84−85 °C [methanol][62]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.3 Hz, 1H), 7.92 (d, J = 2.3 Hz, 1H), 7.68 (d, J = 3.6 Hz, 1H), 7.66 (d, J = 3.3 Hz, 1H), 7.58 (d, J = 9.1 Hz, 1H), 7.35−7.41 (m, 1H), 7.30 (d, J = 7.0 Hz, 1H), 7.10 (dd, J = 2.5, 8.7 Hz, 1H), 3.87 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.0, 55.4, 104.1, 116.7, 120.4, 120.8, 125.6, 126.3, 126.4, 127.7, 129.7, 129.9, 131.1, 131.9, 134.8, 158.4; MS (EI, DIP) m/z 222 (M$^+$, 100), 219 (15), 207 (30), 179 (35), 88 (37); FTIR (KBr, cm^{-1}) 2956, 1616, 1601, 1462, 1231, 1170, 1035, 831; HRMS (EI-TOF) m/z [M]$^+$ for $C_{16}H_{14}O$: calcd, 222.1045; found, 222.1036.

7-Methoxy-1-methylphenanthrene (7g). The title compound was synthesized according to general procedure H using **6h** (2.20 g, 6.52 mmol, 1.0 equiv), Ni(acac)$_2$ (168 mg, 0.654 mmol, 10 mol %), and *i*-PrMgCl·LiCl (0.97 M in THF, 16.8 mL, 16.3 mmol, 2.5 equiv) in Et_2O (90 mL). After standard workup, the residue was purified via column chromatography using heptane/ethyl acetate (9:1) to afford the title compound as a colorless solid (1.14 g, 79%). Further recrystallization from cyclohexane afforded colorless crystals (845 mg, 58%). mp 136 °C (cyclohexane, lit. 134−135 °C[methanol][63]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 8.9 Hz, 1H), 8.50 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 9.1 Hz, 1H), 7.73 (d, J = 9.1 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.40 (d, J = 7.0 Hz, 1H), 7.24−7.33 (m, 2H), 3.98 (s, 3H), 2.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 55.4, 108.3, 117.2, 120.4, 123.4, 124.6, 125.0, 126.2, 126.2, 126.8, 129.8, 130.5, 133.0, 134.8, 158.1; MS (EI, DIP) m/z 222 (M$^+$, 100), 207 (11), 179 (53), 178 (26), 152 (7); FTIR (KBr, cm^{-1}) 2949, 1599, 1270, 1174, 1031, 854, 795; HRMS (EI-TOF) m/z [M]$^+$ for $C_{16}H_{14}O$: calcd, 222.1045; found, 222.1035.

1-Methoxy-8-methylphenanthrene (7h). The title compound was synthesized according to general procedure H using **6i** (1.28 g, 3.79 mmol, 1.0 equiv), Ni(acac)$_2$ (97.5 mg, 0.38 mmol, 10 mol %), and *i*-PrMgCl·LiCl (0.97 M in THF, 8.5 mL, 8.2 mmol, 2.2 equiv) in Et_2O (70 mL). The reaction was left stirring overnight. After standard workup, the residue was purified via column chromatography using heptane/ethyl acetate (9:1) to afford the title compound as a colorless solid (563 mg, 67%). Further recrystallization from cyclohexane afforded colorless crystals (385 mg, 46%). mp 123−124 °C (cyclohexane, lit. 119.8−121 °C [water/methanol][64]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 8.3 Hz, 1H), 8.29 (t, J = 7.9 Hz, 2H), 7.96 (d, J = 9.5 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.54 (t, J = 8.3 Hz, 1H), 7.45 (d, J = 7.0 Hz, 1H), 7.01 (d, J = 7.8 Hz, 1H), 4.05 (s, 3H), 2.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 55.7, 105.5, 115.3, 120.1, 121.4, 122.0, 122.9, 126.0, 126.6, 127.7, 130.0, 131.0, 131.8, 134.8, 155.9; MS (EI, DIP) m/z 222 (M$^+$, 100), 207 (43), 179 (60), 152 (13); FTIR (KBr, cm^{-1}) 2964, 1599, 1263, 1248, 765; HRMS (EI-TOF) m/z [M]$^+$ for $C_{16}H_{14}O$: calcd, 222.1045; found, 222.1051.

1-Fluoro-4-methyl-5-methoxyfluorenone (8). The title compound was synthesized according general procedure B from prepared LDA (DIPA, 185 μL, 1.30 mmol, 1.2 equiv; *n*-BuLi, 2.33 M, 555 μL, 1.30 mmol, 1.2 equiv) in THF (2.5 mL) and **3j** (340 mg, 1.08 mmol, 1.0 equiv) in THF (2.5 mL). The reaction was stirred at 0 °C for 1 h, and after a standard workup, the residue was subjected to column chromatography (pentane/CH_2Cl_2, 1:1). The title compound was obtained as a bright yellow solid (207 mg, 97%). mp 164−167 °C (Et_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dt, J = 1.0, 7.1 Hz, 1H), 7.27 (d, J = 7.4 Hz, 1H), 7.16−7.24 (m, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.78 (t, J = 8.5 Hz, 1H), 3.90 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.9, 55.3, 116.5 (d, J_F = 20.4 Hz), 116.8, 118.7, 130.6, 131.0, 136.4, 140.8, 140.9, 143.8, 154.2, 156.9, 159.5, 190.7; MS (EI, DIP) m/z 242 (M$^+$, 100), 227 (38), 170 (16); FTIR (KBr, cm^{-1}) 2935, 1712, 1616, 1591, 1441, 1273, 1187, 1063; HRMS (EI-TOF) m/z [M]$^+$ for $C_{15}H_{11}FO_2$: calcd, 242.0743; found, 242.0746.

8-Methylphenanthren-1-ol (9a). The title compound was synthesized according to general procedure I with **7h** (222 mg, 1.0 mmol, 1.0 equiv) and BBr_3 (1 M in CH_2Cl_2, 2.0 mL, 2.0 mmol, 2.0 equiv) in CH_2Cl_2 (70 mL). After standard workup, the residue was purified via column chromatography using CH_2Cl_2 to afford the title compound as a colorless solid (118 mg, 57%). mp > 165 °C, dec (DCM, lit. 171−172 °C[65]); ^{1}H NMR (400 MHz, acetone-d_6) δ 9.08 (s, 1H), 8.63 (d, J = 8.3 Hz, 1H), 8.29 (d, J = 8.9 Hz, 1H), 8.00 (d, J = 9.4 Hz, 1H), 7.43−7.57. (m, 3H), 7.10 (d, J = 7.6 Hz, 1H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 20.9, 111.9, 116.1, 122.3, 123.1, 123.2, 123.8,

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127.9, 128.9, 129.5, 132.1, 132.8, 134.0, 136.5, 155.6; MS (EI, DIP) m/z 208 (M^+, 100), 179 (25), 165 (52), 152 (13); FTIR (KBr, cm^{-1}) 3260, 2360, 1600, 1453, 1293, 1246, 767; HRMS (EI-TOF) m/z $[M]^+$ for $C_{15}H_{12}O$: calcd, 208.0888; found, 208.0879.

8-Methylphenanthren-2-ol (9b). The title compound was synthesized according to general procedure I with **7g** (100 mg, 0.45 mmol, 1.0 equiv) and BBr_3 (1 M in CH_2Cl_2, 0.92 mL, 0.92 mmol, 2.05 equiv) in CH_2Cl_2 (35 mL). After standard workup, the residue was purified via trituration with hexanes to afford the title compound as a colorless solid (96 mg, 94%). mp 187−189 °C, melt/dec (hexanes, lit. 187−188 °C [petroleum][66]); ^1H NMR (400 MHz, acetone-d_6) δ 8.75 (s, 1H), 8.65 (d, J = 8.9 Hz, 1H), 8.53 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 9.2 Hz, 1H), 7.70 (d, J = 9.2 Hz, 1H), 7.49 (t, J = 8.1 Hz, 1H), 7.37 (d, J = 7.1 Hz, 1H), 7.34 (d, J = 2.5 Hz, 1H), 7.28 (dd, J = 2.6, 8.9 Hz, 1H), 2.70 (s, 3H) ^{13}C NMR (100 MHz, acetone-d_6) δ 20.9, 113.0, 119.2, 122.1, 125.0, 126.1, 126.6, 127.8, 128.1, 128.4, 131.4, 132.6, 135.3, 136.5, 158.0; MS (EI, DIP) m/z 208 (M^+, 100), 178 (12), 152 (9); FTIR (KBr, cm^{-1}) 3369, 1617, 1468, 1259, 955, 865 cm^{-1}. HRMS (EI-TOF) m/z $[M]^+$ for $C_{15}H_{12}O$: calcd, 208.0888; found, 208.0876.

8-Methylphenanthren-3-ol (9c). The title compound was synthesized according to general procedure I with **7f** (70 mg, 0.31 mmol, 1.0 equiv) and BBr_3 (1 M in CH_2Cl_2, 0.66 mL, 0.92 mmol, 2.1 equiv) in CH_2Cl_2 (10 mL). After standard workup, the residue was purified via column chromatography using CH_2Cl_2 to afford the title compound as a colorless solid (57 mg, 87%). The product is contaminated with approximately 15% cross-coupled compound carried over from **7f** that could not be removed via column chromatography. ^1H NMR (400 MHz, acetone-d_6) δ 9.77 (d, J = 8.5 Hz, 1H), 8.82 (s, 1H), 8.54 (d, J = 8.3 Hz, 1H), 8.19 (d, J = 2.2 Hz, 1H), 7.88 (d, J = 8.6 Hz, 1H), 7.77−7.85 (m, 2H), 7.46−7.58 (m, 2H), 7.28 (dd, J = 2.3, 8.6 Hz, 1H), 2.75 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 21.0, 108.5, 119.0, 121.5, 122.8, 127.5, 127.6, 128.4, 129.6, 131.5, 131.9, 133.0, 134.2, 136.4, 158.4; MS (EI, DIP) m/z 208 (M^+, 100), 178 (11), 152 (8); HRMS (EI-TOF) m/z $[M]^+$ for $C_{15}H_{12}O$: calcd, 208.0888; found, 208.0887.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01300.

^1H and ^{13}C NMR spectra of all new compounds (PDF).

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Notes

The authors declare no competing financial interest.

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